ЖУРНАЛ
АНАЛИТИЧЕСКОЙ
ХИМИИ

Vol. 16, No. 5

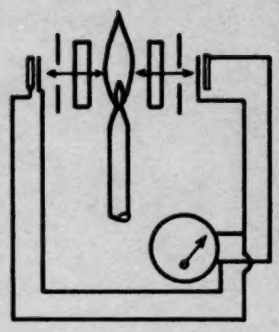
September-October, 1961

JOURNAL OF
ANALYTICAL CHEMISTRY
OF THE USSR

(ZHURNAL ANALITICHESKOI KHIMII)

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU



TECHNIQUES IN FLAME PHOTOMETRIC ANALYSIS

by N. S. Poluéktov

TRANSLATED FROM RUSSIAN

Original published by the State Scientific-Technical Press for Chemical Literature, Moscow

This volume contains a practical and comprehensive survey of the techniques employed and the instruments required for this important rapid analysis method, as well as a brief account of the theoretical principles involved. Experimental procedures and the design of apparatus are discussed at length, making the relevant chapters a valuable manual for all chemists concerned with analytical problems.

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CONSULTANTS BUREAU
ENTERPRISES, INC.
227 W. 17 ST., NEW YORK 11, N. Y.

Vol. 16, No. 5

September-October, 1961

JOURNAL OF
ANALYTICAL CHEMISTRY
OF THE USSR

(ZHURNAL ANALITICHESKOI KHIMII)

A publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

Year and issue of first translation:
Vol. 7, No. 1 Jan.-Feb. 1952

Annual subscription	*$80.00*
Single issue	*20.00*

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JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

Volume 16, Number 5 September-October, 1961

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THE PART PLAYED BY ZIMMERMAN-REINHARDT MIXTURE IN THE PERMANGANOMETRIC DETERMINATION OF IRON

O. A. Songina and S. A. Khodasevich

Kazakh State University, Alma-Ata

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 516-522,
September-October, 1961
Original article submitted July 16, 1960

During titration of iron with permanganate in a hydrochloric acid medium, Zimmerman-Reinhardt solution (we shall henceforth refer to it as Z. R.) which contains manganese sulfate, sulfuric and phosphoric acids is used. Oxidation of chloride ions by permanganate interferes with titration of iron with permanganate in a hydrochloric acid medium when this mixture is not used. The theoretical basis of the action of Z. R. mixture is still the object of discussion. It has been assumed as a basis that oxidation of chloride ions by permanganate is induced by Fe^{2+} ions, while Zimmerman [1a] in 1882, and subsequently Mansho [1b, 2, 3] suggested formation of an intermediate compound of iron which possesses a higher oxidizing capacity than permanganate; this iron compound (assumed to be Fe_2O_5), on breaking down gives "active oxygen" which then reacts with the chloride ions; when Mn^{2+} ions are then introduced into the solution, the "active oxygen" reacts with them, and not with the chloride ions, to give manganese dioxide which behaves as an oxidizing agent with respect to Fe^{2+} ions. Shilov [3] has referred to Wagner's work [4] on the coupled oxidation of hydrochloric acid during the reaction between permanganate and divalent iron; Wagner assumed that oxidation of chloride ions is a side reaction following upon the formation of ferrohydrochloric acid. Shilov on the other hand is of the opinion that oxidation of chloride ions by permanganate in the presence of Fe^{2+} is a typical case of chemical induction, and that the question of whether this process is the main or side reaction depends on the ratio of the concentrations of the acceptor and inductor.

Having considered, and experimentally checked Mansho's hypothesis re the formation of a higher oxide of iron, Shilov arrived at the important conclusion that the active product may be formed not only from the inductor, but also from the actor, if the process does not go to completion i.e., to the most stable oxidation state, but stops at some compound "in an intermediate oxidation state," which on breaking down into compounds of higher and lower oxidation states, behaves as a stronger oxidizing agent than the original material.

This assumption of Shilov has been developed subsequently by many research workers. Thus Basset [3] is of the opinion that there is no need to refer to the formation of a hypothetical compound of iron in a higher valence state, when the whole process can be explained by stepwise reduction of permanganate by Fe^{2+} ions, leading to formation of Mn^{3+} which is also an oxidizing agent with respect to chloride ions; the addition of Mn^{2+} ions lowers the oxidation potential of Mn^{3+} to such an extent that oxidation of chloride ions does not occur. Schleicher in some interesting papers which appeared during 1955 and 1958 [5, 6] develops some ideas which coincide almost completely with N. A. Shilov's hypothesis (Schleicher does not, however, refer to Shilov's work). Schleicher's ideas are almost purely physical in character, and he compares the induction of a chemical reaction with the phenomena of selfinduction and induction which occur in the first order reactions. Schleicher emphasizes that, from a chemical point of view, the phenomenon of selfinduction is a disproportionating phenomenon, and that during redox reactions magnetic fields are formed whose intensity is determined by the number of electrons participating in the process; the existence of these fields and the increase in their intensity which occurs on introducing an additional noninhibited electron process determines the course of the whole redox process. In the given instance, the role of the additional agent is played, according to Schleicher, by the Mn^{3+} ion which is formed reversibly from Mn^{2+} ions and participates in the oxidation of the iron. Since each permanganate ion gives, in the final count, only one Mn^{2+} ion, then in order for the oxidation of iron to proceed sufficiently rapidly, a sufficient amount of Mn^{2+} ions must accumulate, or they must be added specially, this being the case when Z.R. mixture is added. Schleicher considers that the potential of the system Mn^{3+}/Mn^{2+} is less positive than the potential of the system MnO^{-}/Mn^{2+}, but close to it, accordingly oxidation of chloride ions does not occur, and oxidation of iron is not hindered.

Papers were published by Japanese workers in 1959 [7]. It is difficult to judge whether these authors were aware of N. A. Shilov's work but they advance ideas exactly similar to those of N. A. Shilov, i.e., formation of an active agent from the actor. The Japanese workers have introduced a new term "inductive actor" and are of the opinion that in the system MnO_4^- – Fe – HCl, these actors are ions of sexi- and quinquevalent manganese which oxidize the chloride ion to ClO^-; the Mn^{2+} ions introduced with the Z.R. mixture lead to rapid disappearance of these ions as a result of their reduction to Mn^{IV} and Mn^{III}.

In 1954 Schäefer published a paper [8] on experiments which he carried out to demonstrate the effect of Fe^{2+} and Mn^{2+} on oxidation of chloride ions by permanganate. His apparatus consisted of two flasks connected in series with each other; one of these flasks contained a solution of permanganate in hydrochloric acid, while the other contained a solution of potassium iodide and starch. When a stream of nitrogen was passed through the first flask, the solution in the second flask remained colorless; accordingly, the permanganate did not oxidize chloride ions. When a small amount of Fe^{2+} was added to the contents of the first flask, within 10 min, the solution in the second flask acquired a blue color. When, in addition to Fe^{2+}, Mn^{2+} was also added to the contents of the first flask, the solution in the second flask did not turn blue; this indicated that in the presence of Mn^{2+}, chloride ions are not oxidized by permanganate. Schafer makes the important point that when the hydrochloric acid concentration is greater than 0.5 N, direct reaction between permanganate and chloride ions proceeds even in the absence of Fe^{2+} ions.

In order to study the reaction between permanganate and iron we adopted an amperometric method,* using the usual setup with a rotating platinum electrode and a mercury-iodide reference electrode [9]; the potential values given below are referred to this reference electrode (the potential of the mercury–iodide electrode is +0.02 v).

First we "titrated" the supporting electrolytes with permanganate solution (0.05 N) at a potential of +0.7 v, which corresponds to the region for the diffusion current of the reduction of permanganate [9]. Such a technique makes it possible to assess whether any reaction occurs between permanganate and the solution to which it is added. The curves obtained are shown in Fig. 1; curve 1 shows that as the permanganate concentration increases in the supporting electrolyte of sulfuric acid, the current increases linearly (equation $i_d = KC$); this indicates that there is no chemical interaction between permanganate and the supporting electrolyte. Curve 2 (Fig. 1) was obtained for the same sulfuric acid supporting electrolyte, but with addition of hydrochloric acid. In this case the current increases somewhat more slowly and deviates from the straight line $i_d = KC$. This is explained by an interaction between permanganate and hydrochloric acid, which increases with increasing permanganate concentration. As pointed out above, Schäefer [8] has shown that direct (not induced) interaction of permanganate with hydrochloric acid is observed even in the absence of Fe^{2+} ions when the hydrochloric acid concentration exceeds 0.5 N (in our experiments the hydrochloric acid concentration was about 1.5 N, while the total acidity of the solution was about 5 N).

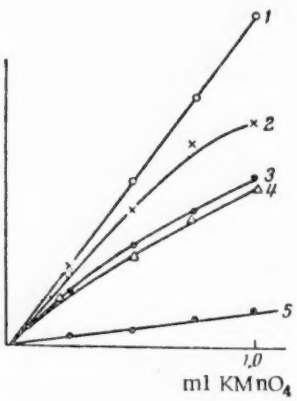

Fig. 1. Titration of supporting electrolytes with permanganate at 0.7 v. 1) Sulfuric acid; 2) sulfuric acid + hydrochloric acid; 3) sulfuric acid + + manganese sulfate; 4) sulfuric acid + hydrochloric acid + + manganese sulfate; 5) Z.R. mixture + hydrochloric acid.

We then titrated solutions of sulfuric acid and mixtures of sulfuric and hydrochloric acids to which were added a small amount of manganese sulfate (curves 3 and 4, Fig. 2). During these titrations, the current which increased immediately on adding each portion of permanganate, decreased with time, and reached a constant value after 30-60 sec (in order to avoid making the diagram too complicated, we have only given the stable current values). The comparatively slow rate at which the current is established indicates a slow reaction between permanganate and Mn^{2+} ions. Shilov has already remarked on this point [2]. The solution acquires a reddish tinge characteristic of Mn^{3+} ions. The fact that the current does not drop to zero but has a definite final value, indicates that the product of the reaction described is capable of being reduced on a platinum electrode at the potential of +0.7 v at which titration is carried out. Since both curves almost coincide (curves 3 and 4, Fig. 1), it is obvious that in both cases – with and without hydrochloric acid – the same process occurs, i.e., oxidation of Mn^{2+} ions by permanganate to Mn^{3+}.

We should like to point out that Selim and Lingane [10] have described a method for producing Mn^{3+} ions by direct titration of divalent manganese with permanganate in a sulfuric acid medium: $Mn^{VII} + 4Mn^{2+} \rightarrow 5\,Mn^{3+}$; formation of Mn^{3+} was established on the basis of a spectrophotometric study of the solutions.

*M. R. Dausheva who carried out all the control tests on titration and polarographic determination helped us considerably in the experimental work.

Figure 1 also includes a titration curve of Z.R. mixture with permanganate (curve 5); in this case again the current is not established immediately; fairly stable values are obtained for the current after 20-30 sec, these values being strictly proportional to the amount of permanganate added. The solution acquires a cherry-red color.

Divalent iron (Mohr's salt) was then titrated with permanganate in the same supporting electrolytes. As Fig. 2 shows, titration in a sulfuric acid supporting electrolyte (curve 1) proceeds without any complications; after the end point, the solution has the rose-violet color characteristic of permanganate. When hydrochloric acid is present (curve 2) the titration curve is "saw-toothed" in shape—after addition of each portion of permanganate the current first increases and then rapidly drops, while the permanganate color disappears and a chlorine odor is observed. It is quite obvious that under such conditions visual determination of the end point is impossible. The interaction between permanganate and hydrochloric acid, as pointed out already, is observable even in the absence of iron; in the presence of the latter the reaction proceeds more intensely because of the Mn^{3+} ions formed from Mn^{2+} ions which appear in solution as a result of the oxidation of the first portions of Fe^{2+} by permanganate. The upper points on curve 2 (Fig. 2) are plotted approximately, since it was impossible to fix their positions accurately: the current drops very rapidly to reach a low constant value which increases slightly as titration proceeds. This current is determined by electrode reduction of the free chlorine which gradually accumulates in the solution.

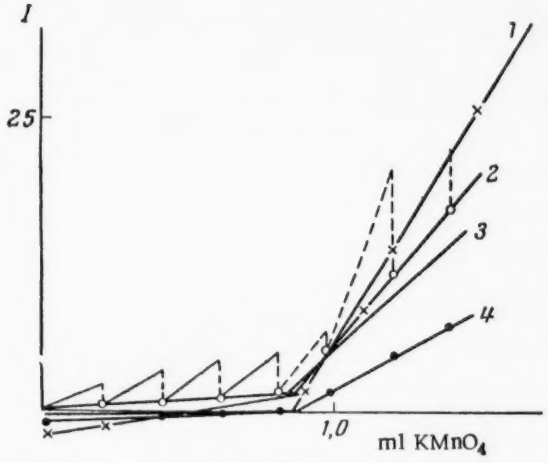

Fig. 2. Titration of divalent iron in different supporting electrolytes. 1) Sulfuric acid; 2) sulfuric acid + hydrochloric acid; 3) sulfuric acid + hydrochloric acid + manganese sulfate; 4) Z.R. mixture + hydrochloric acid.

When manganese sulfate (curve 3) or Z.R. mixture (curve 4) is added to the hydrochloric acid solution of Mohr's salt being titrated, titration proceeds completely normally. The only difference between the curves obtained in this case and when pure sulfuric acid is used as the supporting electrolyte is the lower value of the current after the end point — just as in the case of curve 5, Fig. 1. When only manganese sulfate is present, the solution acquires an orange-red shade, while in the presence of Z.R. mixture it is cherry-red in color. As long ago as 1905, Shilov pointed out that the first product from the reduction of permanganate is manganese oxide Mn_2O_3, which gives a very stable red colored solution with complexing agents. In our case, working with Z.R. mixture, phosphoric acid plays this part. The complex compounds of Mn^{3+} with phosphoric and pyrophosphoric acids have been described several times in the literature [3, 11, 12]. Formation of the phosphate complex of Mn^{3+} also explains the drop in the current which we observed after the end point (compared with the current in the absence of Z.R. mixture); this is obvious when a comparison is made of the polarograms of permanganate in a supporting electrolyte of sulfuric acid (curve 1, Fig. 3) and in a supporting electrolyte of Z.R. mixture (curve 2). According to Belcher and West's results [13] the potential of the pyrophosphate complex of Mn^{3+} (for equimolar ratios of Mn^{2+} and Mn^{3+}) is +1.22 v, consequently Mn^{3+} ions in the presence of phosphate cannot be an oxidizing agent for chloride ions.

Naturally, hydrochloric acid modifies the shape of the permanganate polarogram in the presence of Z.R. mixture, since the anodic current for the oxidation of chloride ions (curve 3, Fig. 3) appears, but even in this case oxidation of chloride ions by trivalent manganese is excluded: this is clear from a comparison of the potentials at which the curves intersect the abscissa in Fig. 3.

Earlier we were able to show that the reaction rate between permanganate and Fe^{2+} ions is greater than that between permanganate and Mn^{2+} ions [12]. Shilov and other workers [1b] have remarked on the relative slowness of this reaction in acid media. Since in our case the acidity of the solution was fairly high (about 5 N), it is only natural to postulate that oxidation of Fe^{2+} occurs first. But, even if it is assumed that the reaction $Mn^{VII} + 4Mn^{2+} \rightarrow 5Mn^{3+}$ proceeds simultaneously with oxidation of iron, it still does not alter the position and is not reflected in the titration results, since the Mn^{3+} formed is immediately reduced by Fe^{2+} ions, i.e., the process postulated by Schleicher occurs [5, 6].

It is usually accepted that the end point of titration of divalent iron by the Z.R. method coincides with the appearance of the red-violet color of permanganate. In actual fact it is the cherry-red color of the phosphate

complex of Mn^{III} which serves as an indicator of the end point. This is a fact which can be readily established even by a visual comparison of the color obtained during such a titration, with the color of a permanganate solution of the same concentration. The high results which are obtained when the usual visual method is used, and which are referred to in textbooks on quantitative analysis [15], are explained, not by the fact that the "oxidation products (i.e., chlorine or hypochlorous acid) react incompletely with divalent iron" [14], but by the fact that the color of Mn^{3+} is considerably less intense than the color of permanganate, so that titration is carried on to a further stage than is necessary until the solution has a clearly defined color. The slow titration recommended in textbooks [15] finds an explanation in the slowness of the reaction between Mn^{2+} and permanganate mentioned above. Using an amperometric method, however, it is also possible to titrate iron in a hydrochloric acid medium with reasonable accuracy, not only in the presence of Z.R. mixture, but even in its absence, since the end point is determined very sharply in this case too.

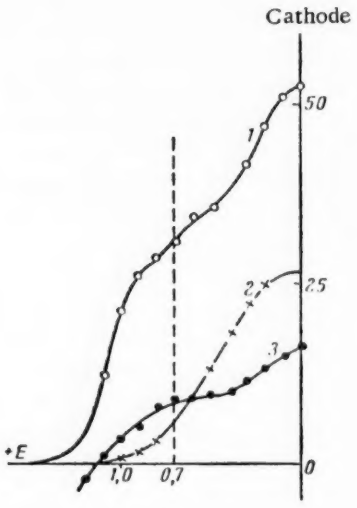

Fig. 3. Polarograms (on a platinum electrode). 1) Permanganate in a sulfuric acid supporting electrolyte; 2) permanganate in a supporting electrolyte of Z.R. mixture; 3) permanganate in a supporting electrolyte consisting of Z.R. mixture and hydrochloric acid. The permanganate content was the same in all cases – 0.6 ml of 0.05 N permanganate in 20 ml.

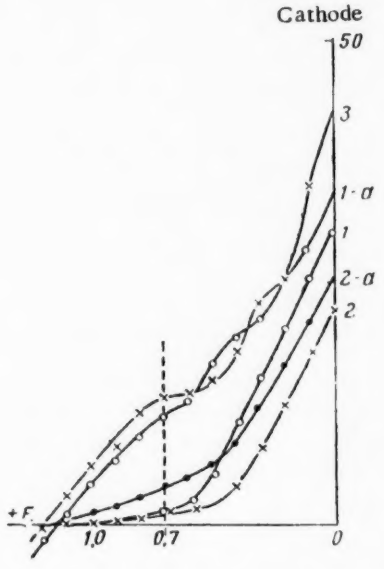

Fig. 4. Polarograms taken during titration of iron with permanganate. 1,2) Before the end point: 1) in a supporting electrolyte of sulfuric and hydrochloric acids; 2) in a supporting electrolyte of Z.R. mixture and hydrochloric acid; 1a and 2a) in the same solutions after the end point in the presence of excess permanganate (0.2 ml of 0.05 N permanganate); 3) chlorine water + Fe in a supporting electrolyte of sulfuric acid.

The amperometric method, in contrast to the usual method, allows one to follow the processes which occur in solution during titration, and which are reflected in the behavior of the indicator electrode (when an appropriate potential is chosen for the latter). In our case in order to assess the changes which occur in the composition of the solution during titration, we took current – voltage curves (polarograms) during titration. The polarograms obtained are shown in Fig. 4; curves 1 and 2 were taken shortly before the end point (when the solution had been titrated to the extent of about 90%); at a potential of +0.7 v, on these curves, one of which corresponds to a solution containing sulfuric and hydrochloric acids, while the second corresponds to a solution of hydrochloric acid and Z.R. mixture, there is observed only an insignificant current corresponding to the incipient reduction of Fe^{3+}, formed from Fe^{2+} during oxidation of the latter. Curves 1a and 2a correspond to curves 1 and 2, but taken after the end point, with 0.2 ml of 0.05 N permanganate solution present in excess. In the case of curve 1a, the solution obtained after the

end point acquires a yellow color (Fe^{3+} in a hydrochloric acid medium), the odor of chlorine is detectable, and the shape of the polarogram indicates reduction of chloride, followed by reduction of Fe^{3+} (at a potential of +0.7 v only reduction of chloride occurs). Curve 1a almost coincides with curve 3 on the same figure, Fig. 4, which was taken specially for comparison in a sulfuric acid solution of chlorine water containing Fe^{3+}. In the case of curve 2a, the solution has a cherry-red color, while the shape of the curve coincides with the polarogram for permanganate in a supporting electrolyte of hydrochloric acid and Z.R. mixture shown in Fig. 3 (curve 2).

Titration curves of different shape can be obtained by choosing another potential for the indicator electrode.

A comparison of our results with published data leads to the following conclusions: the first titration stage – from the beginning of titration to the end point – proceeds in the same way both in a supporting electrolyte of sulfuric acid and in a supporting electrolyte of Z.R. mixture, and consists in the oxidation of Fe^{3+} with permanganate. Comparison of the values of the normal potentials of the systems MnO_4^-/Mn^{2+} and Fe^{3+}/Fe^{2+} (+1.54 and +0.79 v) shows that from an energy point of view this process is quite possible and that there is no need to postulate formation of intermediate oxides of higher valence. In a supporting electrolyte of hydrochloric acid, during the first stage of the titration, oxidation of Fe^{2+} by permanganate also occurs, while after the end point oxidation of chloride ions by excess permanganate occurs; during the first stage of titration, in parallel with oxidation of iron, there also occurs, but only to a very small extent as a side reaction, formation of free chlorine, which gradually increases as the end point is approached. Proof of the fact that this process is a side reaction is that the titration end point is very sharp in this case too, and coincides with the end point in the absence of hydrochloric acid. Presumably, oxidation of chloride ions during the first stage of the titration is effected by Mn^{3+} ions formed by the oxidation of Fe^{2+} by permanganate, while after the end point oxidation is effected directly by the permanganate. When Z.R. mixture is present, i.e., in the presence of a large excess of Mn^{2+} ions, a reaction occurs between the latter and permanganate, and not between the chloride ions and permanganate. This reaction leads to the formation of Mn^{3+}, the stability of which in the given instance is ensured by the presence of phosphoric acid. From an energy point of view, the reaction between permanganate and Mn^{2+} ions present in large excess, and which, accordingly lower the potential of the system Mn^{3+}/Mn^{2+}, is more efficient than the oxidation of the chloride ions, since the potential of the system Mn^{3+}/Mn^{2+} is less positive than the potential of the system $Cl_2/2Cl^-$, particularly in the presence of phosphate which complexes the Mn^{3+} ion.

SUMMARY

An amperometric method has been used for studying titration of divalent iron with permanganate in sulfuric, and hydrochloric acid solutions and in hydrochloric acid solutions containing Zimmerman-Reinhardt mixture.

It has been shown that in all three supporting electrolytes, before the end point is reached, titration of iron with permanganate consists in the direct oxidation of Fe^{2+} ions by permanganate.

Normal visual titration is impossible in a hydrochloric acid medium because after the end point the chloride ions start to react with permanganate and lead to decolorization of the solution.

Addition of Zimmerman-Reinhardt mixture eliminates this phenomenon, since in this case the permanganate oxidizes the Mn^{2+} ions and not the Cl^- ions; the Mn^{3+} formed which is complexed by phosphate is responsible for the stable cherry-red color of the solution, this color serving as an indicator during visual titration.

It has been shown that by using an amperometric method it is possible to titrate iron with permanganate in a hydrochloric acid medium without adding Zimmerman-Reinhardt mixture.

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THE SOLUBILITY PRODUCT OF ETHYLENEDIAMINETETRACETIC ACID

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 523-526, September-October, 1961
Original article submitted November 30, 1960

The solubility of ethylenediaminetetracetic acid (EDTA)* has been determined by a number of research workers [1-5]. The solubility product has, however, not hitherto been calculated. Using published data on the solubility of EDTA we have calculated $Z_{sol.\ EDTA}$.

Klygin, Smirnova, and Nikol'skaya [4] have established the relationship between the solubility of EDTA and pH at 25°. They concluded that a cation of the ammonium type H_6Y^{2+} exists, and calculated its dissociation constant. They did not take into account, however, the possibility of successive addition of protons to the EDTA molecule, and the presence of its dissociation product (H_3Y^-). We have taken these factors into account in our calculations. We used the data on the solubility of EDTA in hydrochloric acid solutions for our calculations ([4] table).

At pH < 2, the concentration of H_2Y^{2-}, HY^{3-}, and Y^{4-} is negligible and can be ignored. One must, however, take into account possible addition compounds formed by addition of protons to the EDTA molecule. Tillotson and Stavely [6] who calculated the dissociation constant of the ion H_5Y^+, were the first to point out the existence of such cations in solution. They also assumed formation of a H_6Y^{2+} ion, but were unable to prove this experimentally. Klygin [4], as indicated above, denies the existence of the H_5Y^+ ion, and states that two hydrogen ions add on simultaneously to the amino groups in EDTA. Palei and Udal'tsova [5] also postulate formation of the H_6Y^{2+} ion in solution. In addition, these authors isolated from strongly acid (3 N HCl) solutions of EDTA, a sparingly soluble compound $[H_6Y]Cl_2$ or $H_4Y \cdot 2HCl$ (and the analogous sulfate of EDTA). We did not take the possibility of the formation of such compounds into account in our calculations, since we used solubility values obtained at fairly high pH values (> 0.8).

Taking what has been said above into account, the solubility of EDTA is equal to

$$S = \sum_{i=3}^{6} [H_iY^{i-4}]. \tag{1}$$

The concentrations of the individual ionic (and molecular) forms of EDTA are equal to:

$$\left.\begin{aligned} [H_3Y^-] &= \frac{[H^+]^3[Y^{4-}]}{k_2k_3k_4}, \\ [H_4Y^0] &= \frac{[H^+]^4[Y^{4-}]}{k_1k_2k_3k_4}, \\ [H_5Y^+] &= \frac{[H^+]^5[Y^{4-}]}{k_0k_1k_2k_3k_4}, \\ [H_6Y^{2+}] &= \frac{[H^+]^6[Y^{4-}]}{k_{00}k_0k_1k_2k_3k_4}, \end{aligned}\right\} \tag{2}$$

where k_1, k_2, k_3, and k_4 are the respective dissociation constants of EDTA and

$$\left.\begin{aligned} k_0 &= \frac{[H^+][H_4Y]}{[H_5Y^+]}, \\ k_{00} &= \frac{[H^+][H_5Y^+]}{[H_6Y^{2+}]}. \end{aligned}\right\} \tag{3}$$

* Designated as H_4Y.

The solubility of EDTA is determined by the formula

$$L_p = [H^+]^4 [Y^{4-}]. \quad (4)$$

From relations (1), (2), and (4) by algebraic transformation we obtain:

$$S \cdot [H^+] = \frac{L_p}{k_2 k_3 k_4} + \frac{L_p}{k_1 k_2 k_3 k_4} \cdot [H^+] + \frac{L_p}{k_0 k_1 k_2 k_3 k_4} \cdot [H^+]^2 + \frac{L_p}{k_{00} k_0 k_1 k_2 k_3 k_4} \cdot [H^+]^3. \quad (5)$$

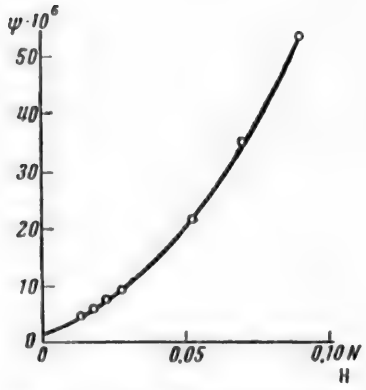

Fig. 1. Graphical determination of B_0.

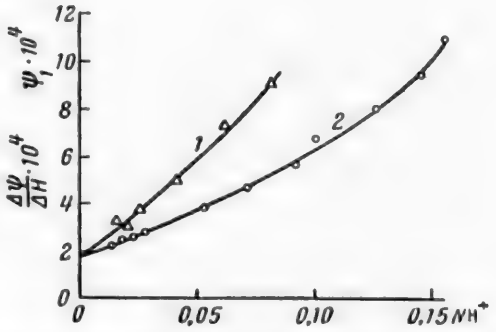

Fig. 2. Graphical determination of B_1. 1) $\Delta\Psi$ per ΔH; 2) Ψ_1.

Designating $[H^+]$ by H and $S \cdot [H^+]$ by Ψ and introducing the appropriate designations for the coefficients in front of $[H^+]$, equation (5) can be represented in the form

$$\psi = B_0 + B_1 \cdot H + B_2 \cdot H^2 + B_3 \cdot H^3. \quad (6)$$

We determined the coefficients of this equation graphically. Figure 1 shows the curve relating Ψ and H. By extrapolating the curve to zero hydrogen ion concentration we obtained the value of B_0:

$$H \to 0, \ \psi \to B_0 = 1{,}8 \cdot 10^{-6}.$$

We used the values of the dissociation constants of EDTA determined by Schwarzenbach at 20° [7] for calculating the value of L_{sol}. Errors arising from temperature differences were not taken into account in view of the large errors arising from the inconstancy of the ionic strength in the experiments used.

$$L_{sol} = k_2 k_3 k_4 \cdot B_0 = 1{,}45 \cdot 10^{-25}.$$

From (6) we find that

$$\frac{d\psi}{dH} = B_1 + 2B_2 \cdot H + 3B_2 \cdot H^2. \quad (7)$$

The curve $\Delta\Psi/\Delta H - H$ is shown in Fig. 2 (curve 1), where H designates the mean point of the range for which the slope $\Delta\Psi/\Delta H$ is calculated.

$$H \to 0, \ \frac{\Delta\psi}{\Delta H} \to B_1 = 1{,}8 \cdot 10^{-4}.$$

We also determined B_1 by extrapolating the function

$$\psi_1 = \frac{\psi - B_0}{H} = B_1 + B_2 \cdot H + B_3 \cdot H^2. \quad (8)$$

to H = O (Fig. 2, curve 2): $\Psi_1 \to B_1 = 1{,}8 \cdot 10^{-4}$.

From which

$$L_{sol} = k_1k_2k_3k_4 \cdot B_1 = 1{,}45 \cdot 10^{-26}$$

The same value of L_{sol} was obtained as that derived from B_0. Next the following function was plotted (Fig. 3)

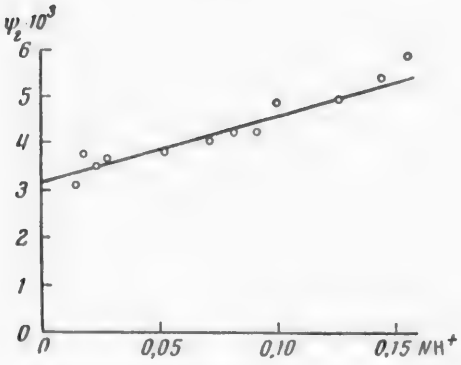

Fig. 3. Graphical determination of B_2 and B_3.

$$\psi_2 = \frac{\psi_1 - B_1}{H} = B_2 + B_3 \cdot H. \qquad (9)$$

$$H \to 0,\ \psi_2 \to B_2 = 3{,}2 \cdot 10^{-3}.$$

The fact that B_2 differs from zero indicates the existence of a cation of the ammonium type H_5Y^+. We calculated the value of k_0 from the value found for B_2:

$$k_0 = \frac{L_{sol}}{k_1k_2k_3k_4B_2} = 5{,}6 \cdot 10^{-2},\ pk_0 = 1{,}25.$$

Tillotson and Stavely [5] found $pk_0 = 1.55 \pm 0.13$ for 20° at $\mu = 0.1$.

It follows from (9) that:

$$\frac{\Delta\psi_2}{\Delta H} = B_3. \qquad (10)$$

The slope of the straight line in Fig. 3 differs from zero. Accordingly, the cation H_6Y^{2+} exists. The slope was found to be equal to $B_3 = 1.4 \cdot 10^{-2}$. From which

$$k_{00} = \frac{L_{sol}}{k_0k_1k_2k_3k_4B_3} = 2{,}2 \cdot 10^{-1},\ pk_{00} = 0{,}66.$$

The total dissociation constant of a cation of the ammonium type H_6Y^{2+} is given by

$$K = \frac{[H_+]^2[H_4Y]}{[H_6Y^{2+}]} = k_0k_{00} = 1{,}23 \cdot 10^{-}.$$

This value was found to be in agreement with that calculated by Klygin, Smirnova, and Nikol'skaya [4]. These authors, however, did not take into account the existence of the H_5Y^+ ion([4], equation (4)]. Obviously, the concentration of undissociated molecules which they calculated $[H_4Y] = 3.56 \cdot 10^{-4}$, was greater than the solubility of EDTA for a series of pH values.

It is interesting to compare the calculated value of $L_{sol,\ EDTA}$ with that calculated on the basis of the results of Mechelynck and Schietakatte [1]. These results, presumably, relate to room temperature. The solubility of EDTA was determined over the pH range 1.13-7.32.

In our calculations we took into account all possible fragments of EDTA, apart from Y^{4-}. An equation similar to equation (5) was derived. $L_{sol,\ EDTA}$ was calculated for each pH value, by means of this equation.

It is clear from the table that the calculated values of L_{sol} are constant over the pH range 1.13-4.67. At pH 6.12 and 7.32, obviously low values of L_{sol} were obtained (three and six orders lower respectively). This apparently indicates changes in the composition of the precipitate.

The mean geometrical value [8] of the calculated values of L_{sol} is equal to $4.0 \cdot 10^{-26}$. This value is less than the value obtained for L_{sol} on using the results of Klygin et al. The deviations are obviously the result of difference in temperature.

It is impossible to calculate the values of $L_{sol,\ EDTA}$ on the basis of the results given by the Japanese workers [2, 3] and by Palei and Udal'tsova [5] since these authors did not measure the pH of the solution.

Calculations of $L_{sol.\ EDTA}$ on the Basis of Mechelynck and Schietakatte's Results

pH	S, M	$L_{sol} \cdot 10^{26}$
1.13	$3.07 \cdot 10^{-4}$	6.5•
1.97	$1.73 \cdot 10^{-4}$	5.6•
2.86	$7.18 \cdot 10^{-4}$	3.0
3.31	$3.33 \cdot 10^{-3}$	2.4
3.80	$3.90 \cdot 10^{-2}$	3.4
4.11	$3.46 \cdot 10^{-1}$	5.5
4.67	1.87	3.2
6.12	1.81	$2.1 \cdot 10^{-3}$••
7.32	2.42	$1.4 \cdot 10^{-6}$••
Mean		4.0

• $\overline{pk_0}$ = 1.55 was used in the calculations [7]. The presence of H_6Y^{2+} was not taken into account.

•• Not taken into account when the mean value was determined.

SUMMARY

Using published data on the solubility of ethylenediaminetetracetic acid, the value of the solubility product of this acid has been determined. At 25° $L_{sol} = 1.45 \cdot 10^{-25}$.

Calculations have demonstrated the existence of two products which are formed by the successive addition of protons to the EDTA molecule, they are H_5Y^+ and H_6Y^{2+}. Their dissociation constants have been calculated (at 25°); they were found to be equal to $pk_0 = 1.25$ and $pk_{00} = 0.66$ respectively.

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A METHOD FOR CORRECTING THE RELATIVE INTENSITY OF ANALYTICAL PAIRS OF LINES IN AN ARC DISCHARGE

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 527-531, September-October, 1961
Original article submitted November 28, 1960

In previous papers [1, 2] we discussed the reasons for the displacement of the calibration curve, and arrived at a formula on the assumption that the terms in the equation, which include the degree of ionization of the atoms $\underline{x}$ and x' of the test and main element respectively, act in opposite directions for atomic and ionic pairs of lines. Such an assumption, as will become evident from what follows, proved to be erroneous. Using Sach's formula and Unzold's nomogram [3], it is possible to determine approximately the relationship between the values of log (x_n/x'_n), log $(1-x_n/1-x'_n)$ and the plasma temperature for tin which has an ionization energy of ϵ = 7.33 ev (impurity) and copper with ϵ' = 7.72 ev (the main element), which are shown in Fig. 1. When copper is the impurity element and tin the main element, then the curves for the values of log (x_n/x'_n) and log $(1-x_n/1-x'_n)$ change places like a mirror image relative to the abscissa. The extent of the two-fold ionization of the atoms must be taken into account at the temperature of the plasma spark, and this was not done in the given instance.

As Fig. 1 shows, the relative content of tin and copper ions increases with decreasing plasma temperature. At the same time the relative content of their neutral atoms also increases. Accordingly, there is no basis for changing the sign in the equation before the term [1]. It is also clear from the diagram that at low temperatures the value of

$$\lg\frac{1-x_n}{1-x'_n} - \lg\frac{1-x_0}{1-x'_0} \qquad (1)$$

is less than the experimental error $\Delta S = \pm 0.02$. For example, on dropping the plasma temperature from 6000 to 5000° in the case of the elements Ca–Cu this difference is 0.008, while on dropping the temperature from 7000 to 6000° for Cr–Cu the difference is 0.016. Accordingly, the difference (1) can be excluded from consideration during a discussion of the results obtained by means of an arc discharge in the case of nonalkali metals. In such a case, the formulas for the fractional displacements of the curves assume the following forms:

1) Because of changes in the value of the exponential function

$$\frac{1}{n} - \frac{1}{T_0} = \frac{k(\delta S'_n - \delta S''_n)}{0{,}43\cdot\gamma(|\Delta E' + \Delta E''|)}. \qquad (2)$$

2) Because of changes in the relative content of the ions

$$\lg\frac{x_n}{x'_n} - \lg\frac{x_0}{x'_0} = \frac{\delta S'''_n - \delta S'_n}{\gamma} + \frac{(\Delta E'' - \Delta E^a)(\Delta S'_n - \delta S''_n}{\gamma(|\Delta E'| + \Delta E'')}. \qquad (3)$$

3) As a result of changes in the relative rate of evaporation of the elements being compared and their diffusion in the plasma

$$\lg\frac{d_n}{\beta_n} - \lg\frac{d_0}{\beta_0} = \frac{\delta S'_n}{\gamma} + \frac{\Delta E^a(\delta S'_n - \delta S''_n)}{\gamma(\Delta E' + \Delta E'')} \qquad (4)$$

where $\delta S_n^{\blacksquare}$, $\delta S_n'$ and $\delta S_n^{\bullet}$ are the values of the total displacement of the curve respectively for the ionic pairs of lines, the atomic pairs of lines with $\Delta E' < 0$, and the atomic pairs of lines with $\Delta E^{\bullet} > 0$, on dropping the plasma temperature from T_0 to T_n (for details see [1, 2]); ΔE is the difference in the excitation energy of the corresponding pairs of lines. The fractions of the displacement which can be attributed to each cause have been established experimentally, and confirm the correctness of the theoretical conclusions.

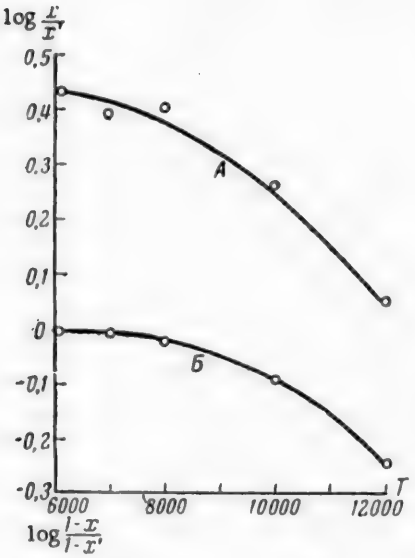

Fig. 1. Curves for the relationships between relative content of A) Ions, log (x_n/x'_n) and B) neutral atoms Sn–Cu, log $(1-x_n/1-x'_n)$ and plasma temperature.

The extents to which the curve is displaced as a result of the action of the corresponding factor were established from the experimentally established total displacement of the curve for three pairs of lines at a known concentration of the test element in standards. In practice, as a rule, the reverse is met – determination of the concentration of an element on the basis of the relative intensity of the analytical pair of lines emitted, the solution of which is set forth in the present article. Such a problem can be resolved with a reasonable accuracy by using calibration curves, on the condition that one takes into account the change in the relative intensity of the radiation of the analytical pair of lines arising from a possible change in the degree of ionization of the atoms of the element being compared, in their relative evaporation rates, and in the value of the exponential function caused by changes in the discharge conditions.

As soon as formulas (2-4) for calculating the fractional displacements of the curve have been established theoretically, and their correctness has been confirmed experimentally, the problem posed can be partially solved in the following manner, in the case of the determination of nonalkali metals in an arc discharge. We represent the calibration curves of the corresponding pairs of line one above the other, preserving their experimentally determined slopes, the values of their displacement, and the arrangement of the points along the abscissa as shown in Fig. 2. The arrangement of the points along the ordinate is arbitrary. The differences in the blackening density of the analytical pairs of lines are plotted along the ordinate, while the logarithm of the relative concentration of the test element is plotted along the abscissa.

The straight lines $A^{\bullet}$ and A' represent calibration curves for the atomic pairs of lines of tin and copper respectively with positive and negative ΔE values. They were obtained in the absence of an oxide film and under conditions of weak reabsorption of the spectral lines. The true path of the curve for the ionic pair of lines with a negative value of $\Delta E^{\blacksquare}$ is shown by the dot-dash line. Its slope is different from the slopes of the curves for the atomic pairs of lines. The angle between them is ω. To keep the whole thing in perspective we depict this curve $A^{\blacksquare}$ in parallel with curves $A^{\bullet}$ and A'. The continuous straight lines A_0 were obtained using binary standards, while the dotted lines A_n were obtained using standards containing 10% sodium. We shall denote the values of the displacement of the curves for the atomic pairs of lines with a positive value of $\Delta E^{\bullet}$ by $A_0^{\bullet}A_n^{\bullet} = B_0^{\bullet}B_n^{\bullet} = \delta S_n^{\bullet}/\gamma$, for the atomic pair of lines with a negative value of $\Delta E'$ by $A_0'A_n' = B_0'B_n' = \delta S_n'/\gamma$, and for the ionic pair of lines by $A_0^{\blacksquare}A_n^{\blacksquare} = C_0^{\blacksquare}E^{\blacksquare} = \delta S_n^{\blacksquare}/\gamma$. The points $A_0^{\bullet}$, A_0', and $A_0^{\blacksquare}$ are the values of the relative intensity of the corresponding analytical pairs of lines for a certain tin concentration. They lie on the curves constructed on the basis of standards of a binary composition. Addition of 10% sodium to the standards leads to an increase in the relative intensity of the pairs of lines, despite the fact that the relative content of tin and copper remains the same.

The relative intensities of the analytical pairs of lines for samples containing sodium are denoted by $A_n^{\bullet}$, A_n' and $A_n^{\blacksquare}$. They lie on the curves constructed on the basis of standards containing 10% sodium. Were these values of the relative intensity of the pairs of lines plotted on the curves obtained with binary standards, then points $B_0^{\bullet}$, B_0', and D or $B_0^{\blacksquare}$ would correspond to them. Determination of the concentration of tin in a sample on the basis of these points would lead to different results for different pairs of lines.

As Fig. 2 shows, the concentration of the elements found in a sample proves to have different values and is high, and it becomes higher on switching from the curve for the atomic pair of lines with $\Delta E^{\bullet} > 0$ to the curve for the atomic pair of lines with $\Delta E' < 0$, and to the curve for the ionic pair of lines. It is also clear from the

diagram that the apparent increase in concentration of the element being determined, when it is determined by the curves for different pairs of lines, points to an increase in the relative intensity of the emission of these pairs of lines or to a displacement of their calibration curves upwards on adding sodium to a sample.

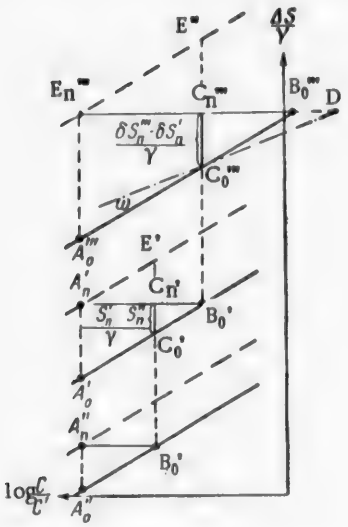

Fig. 2. Schematic diagram of the curves relating the relative intensity of line pairs and the concentration of tin relative to copper content: $A^{"}$ = Sn I 2429 − Cu I 2492 with $\Delta E^{"} > 0$, A' − Sn I 2429 − Cu I 2766 with $\Delta E' < 0$ and $A^{""}$ − Sn II 2246 − Cu II 2242 with $\Delta E^{""} < 0$. The continuous lines were obtained using binary standards; the dotted lines were obtained using standards containing 10% sodium.

In the case under consideration the relative intensity of the spectral lines increases on adding sodium to a sample, both as a result of an increase in the content of the tin being determined (α) relative to copper (β) the main element in the plasma, and as a result of an increase in the relative content of their ions. Addition of sodium to a tin-chromium sample, made from the respective chlorides, leads, on the other hand to a decrease in the content of the test tin (α) relative to the main element chromium (β) in the plasma, and leads to a decrease in the relative content of their ions, as a result of which the relative intensity of the pairs of lines decreases. In such a case the concentration, determined on the basis of the relative intensities of the lines, and on the basis of the curves of binary standards, proved to be low. Accordingly, it is possible, to establish accurately, on the basis of the increase or decrease in the concentration of an element, which is observed on switching from the curves of one pair of atomic lines to the curve for another pair of atomic or ionic lines, whether the relative intensity of the corresponding pairs of lines increases or decreases as the result of changes in the content of the ternary components in the sample, or in the discharge conditions. If it is possible thereby to determine the amount by which the relative intensity of the analytical pairs of lines changes as a result of third component effects, or as a result of changes in the discharge conditions, it should be possible to develop a method for determining the contents of elements in any samples on the basis of binary standards.

In order to determine the amount by which the relative intensity of the analytical pairs of lines changes as the result of these respective reasons, lines are drawn from points $B_0^{"}$, B_0', and $B_0^{""}$ parallel to the ordinate and abscissa. As a result, a series of right angled triangles is obtained. Let us compare triangles $A_n^{"}B_n'B_0^{"}$ and $A_n'E'B_n'$. On comparing them it is evident that the angles $\angle B_0^{"}A_n^{"}B_n^{"} = \angle B_n'A_n'E'$, $\angle A_n^{"}B_n^{"}B_0^{"} = \angle A_n'DB_n'$, $\angle B_n^{"}B_0^{"}A_n^{"} = \angle D'B_n'A_n'$ and sides $A_n^{"}B_0^{"} = A_n'B_n'$, $A_n^{"}B_n^{"} = A_n'D'$ are equal. Since all the corresponding angles and the two sides of the triangles compared are equal, it follows that their third sides are also equal, viz: $C_n'C' = B_0^{"}D_n^{"} = \delta S_n^{"}/\gamma$. Consequently

$$B_0'B_n' = \frac{\delta S_n' - \delta S_n^{"}}{\gamma}. \tag{5}$$

This accordingly gives a method for determining the value of $(\delta S_n' - \delta S_n^{"}/\gamma)$ on the basis of the curves for binary standards. Having experimentally determined the numerical value of the relation (5), it is possible by means of formula (2) to find the value by which the relative intensity of the respective pairs of lines changes when the values of the exponential function change as a result of a decrease or an increase in the plasma temperature.

The triangles $A_n'B_n'B_0'$ and $A_n^{""}D^{""}B_n^{""}$ are compared next. It is clear from the diagram that their corresponding angles and two sides are equal, so that their third sides are also equal, thus: $D^{""}B_n^{""} = B_n'B_0' = \delta S_n'/\gamma$. We then obtain

$$B_n^{'''}B_0^{'''} = \frac{\delta S_n^{'''} - \delta S_n'}{\gamma}. \tag{6}$$

In this way a method is also found for determining the value of $\delta S_n^{""} - \delta S_n'$. If the smaller slope of the curves for the ionic pairs of lines is taken into account, then

$$B_n^{'''}B_0^{'''} = \frac{\delta S_n^{'''} - \delta S_n'}{\gamma \cdot \cos\omega}. \tag{7}$$

Knowing the numerical values of relationships (5) and (7), it is possible, by using formula (3), to calculate the value by which the relative intensity of the ionic pairs of lines alters as a result of changes in the relative content of the ions of the elements being compared, following upon a decrease or increase in the plasma temperature.

After correcting the relative intensity of the corresponding pairs of lines by the respective values (2 and 3), the accuracy with which the concentration of the elements can be determined on the basis of the given curves is considerably increased. In this way it has been found possible to solve the problem of eliminating the error in determining the concentration of a test element which arises as a result of changes in the temperature of the arc plasma, such temperature changes being possible when the discharge conditions or the content of certain third components in the sample alter. As Semenova has shown [4] the error in determining the concentration of a test element may be high because of such changes.

Unfortunately, the question of how it is possible to determine the extent of the change in the relative intensity of the pairs of lines following upon changes in the relative content of the elements being compared in the plasma (4), still remains unsolved. If this problem could be solved as well, it should be possible to attach a programmer to the multichannel DFS-10 apparatus, and determine the concentration of the elements in alloys of different types automatically on the basis of one calibration curve. As is evident from Fig. 1, at high temperatures sparks occur in the plasma, and the value (1) is higher. This fact complicates solution of the problem posed still further.

In conclusion I should like to express my warmest thanks to M. A. El'yashevich for his advice.

SUMMARY

A method is given for calculating the change in the relative radiation intensity of an analytical pair of lines, caused by a decrease or an increase in the arc plasma temperature following upon changes in the discharge conditions. The values $(\sigma S'_n - \sigma S''_n/\gamma)$ (5) and $(\sigma S''_n - \sigma S'_n/\gamma)$ (6) are determined from the calibration curves for the two pairs of atomic lines and one pair of ion lines. Subsequently, it is possible, by means of formulas (2) and (3), to determine the values of the change in the relative intensity of the pair of lines following upon changes in the value of the exponential function and in the degree of atom ionization.

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EXCITATION CONDITIONS OF THE SPECTRA OF ELEMENTS IN A PLASMA GENERATOR AND THE APPLICATION OF THE LATTER FOR THE SPECTROGRAPHIC ANALYSIS OF TITANIUM ALLOYS

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 532-537, September-October, 1961
Original article submitted November 30, 1960

During the spectrographic determination of impurities in titanium metal or during the control of the content of alloying elements added to titanium alloys, it is always necessary to take into account the possibility of uneven distribution of the elements to be determined in the test material. This gives rise to additional errors, and, in some cases, excludes the possibility of using an arc or spark excitation source. During analysis of titanium alloys the problem is also complicated by difficulties associated with the preparation of standard samples. Accordingly, in most current techniques [1-3], determination of impurities in titanium and in its alloys is carried out after converting titanium into its dioxide, the latter being then analyzed spectrographically by excitation in an arc. A much more radical approach for overcoming such difficulties is to resort to analyzing solutions, which, in the case of titanium alloys can be realized with exceptional ease and simplicity. Several such methods have been described [3-6], in which the metal is brought into solution, and the latter subsequently analyzed with a porous or rotating electrode with excitation of the spectrum in a spark.

Great possibilities have been opened up thanks to the introduction into spectrographic practice [7, 8] of a new excitation source, the so-called plasma generator, which allows, as experience has shown [7, 9], the accuracy and reliability of the spectrographic determination of elements in solution to be increased considerably.

The present article is devoted to a technique which we have developed for the analysis of titanium alloys by means of a plasma generator. Results of a study of certain characteristics of the new excitation source are also included.

Study of the excitation conditions of the spectra of various elements in the source. A plasma generator adapted for the analysis of solutions, and whose design has already been described earlier [9] was used in the work.

An attempt was made during a series of systematic experiments to establish the way in which the blackening of the analytical lines of various elements changes along the length of the source stream, and to study the effect of certain factors, which influence the excitation conditions of the atoms of the elements in the plasma, on the form and spatial distribution of these curves. Of these factors we first examined the ionization potential of the elements and the excitation energy of their emission lines, the source temperature, and the effect of cations and anions. In addition, of no little interest was an examination of the effect on the excitation conditions of the elements, of the addition of organic materials to the test solutions, in paricular addition of ethanol, the presence of which, as our preliminary observations have shown [9], is reflected in the radiation intensity of the line of an element in a plasma stream.

The results of these experiments are shown in Figs. 1-6. An examination of these leads to the following conclusions:

1) A decisive effect on the shape and the position of the maxima on the curves relating line blackening of various elements to the distance from the base of the plasma generator stream (Fig. 1) is shown by the value of the excitation energy of these lines. The ionization potential of the element, has, in practice almost no significance. With decreasing excitation energy of the emission lines, there is observed, as a rule, a widening in the maximum of the curves considered, while its position is shifted along the length of the stream away from the base. This

deformation in the shape of the curves can be particularly clearly followed in the case of the lines of the alkali elements (Fig. 2.

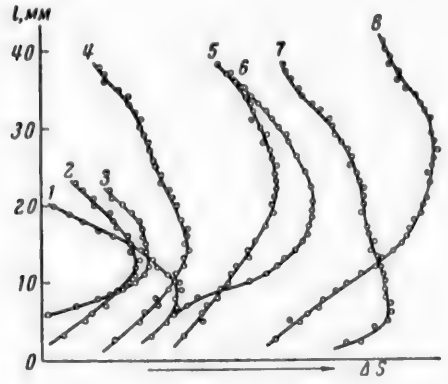

Fig. 1. Change in line blackening (ΔS) of various elements (compared with the blackening of the spectrogram background) along the length of the plasma generator stream. l is the distance in mm from the base of the stream. 1) For the line Fe II 2410.5 (5.25 ev); 2) Fe I 3019 (5.06 ev); 3) Cr I 3017.6 (5.1 ev); 4) Al I 2652.5 (4.66 ev); 5) Ti II 3234.5 (3.9 ev); 6) V I 3185.4 (4 ev); 7) Zn I 3345.0 (7.78 ev); 8) Cr I 4254.4 (2.9 ev). The excitation potentials of the lines are given in brackets. The relative position of the curves along the abscissa is arbitrary.

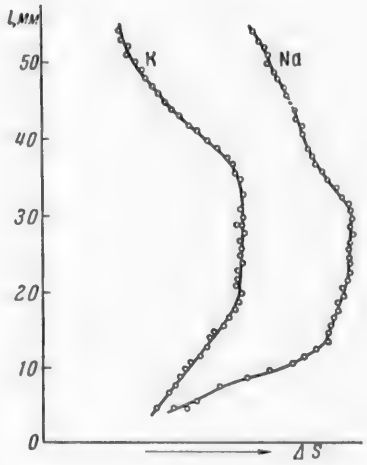

Fig. 2. Change in blackening of the lines K I 3446.7 (3.60 ev) and Na I 3302.3 A (3.75 ev) along the plasma generator stream. The relative position of the curves along the abscissa is arbitrary.

The position of the maximum and the shape of the curves considered are very close (e.g., curves 2 and 3, or 5 and 6 in Fig. 1) in the case of the lines of various elements with similar excitation potentials. On the other hand, when there is an appreciable difference in the values of the excitation potentials of the lines, even of the same element (curves 3 and 8 in Fig. 1), the shape of these curves and the position along the plasma stream corresponding to the blackening maximum of the respective lines can differ from each other to a very considerable extent. This fact must be borne in mind when choosing the analytical lines of the elements, and the optimum conditions for carrying out analyses of various objects. On the one hand, the effect indicated sets certain limitations and can, for example, sometimes complicate the choice of reference lines which are suitable under other relationships, while on the other hand, as a result of the possibility of a spatial separation of the maxima of successfully chosen analytical lines of various elements along the plasma stream, it opens up the possibility of artificially increasing the line intensity of certain elements at the expense of the weakening of others by correct choice of the operating part of the plasma stream.

2) Anions do not affect the character of the distribution of line intensity of the elements in a plasma generator stream (Fig. 4).

Cations of other elements present in solution, judging from available data (Fig. 3), may sometimes give rise to a small (and seldom realized from a practical point of view) shift in the original curves. This question, however, deserves a wider and more systematic study.

3) In order to have an idea of the nature of the change in the excitation conditions of the lines of the elements on moving along the plasma generator stream, a study was made of the relationship between the relative intensity of the spark and arc lines of iron (or for simplicity ΔS) and the distance to the base of the stream (l), in which various sections of the radiating plasma were projected on the spectrograph slit. It was established during the course of this study (Fig. 5) that there is a linear decrease in the difference in the blackening of the lines of the fixed pair used, indicating thereby an uniform decrease in the source temperature as one moves along the stream from its base to its periphery.

Addition of ethanol (50%) to the solution does not destroy the general features of the relationship between the temperature of a corresponding zone of the source plasma and its position in the stream (curve w, Fig. 5), but leads to an experimentally fixed decrease in the source temperature as a whole. In accordance with this, addition of alcohol also has an effect on the position of the maximum and on the shape of the curves relating blackening of the analytical lines of test elements to distance of the various zones of the stream from the base (Fig. 6). As one might expect, in view of what has been said above, the presence of alcohol in solution leads to an expansion of the original curves, and to the displacement of their maxima toward the base of the stream. A certain increase in the intensity of the analytical lines of the elements is also observed, the magnitude of the increase being dependent on the values of the excitation potentials of the elements; on an average it usually amounts to 1.5-2 times.

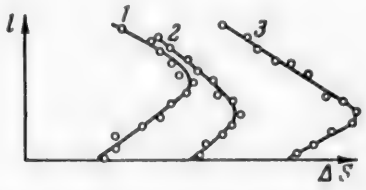

Fig. 3. Effect of foreign cations present in the plasma on the nature of the relationship between the intensity of the line Fe I 2719.02 A and the distance to the base of the plasma stream. 1) In absence of other cations in the plasma (iron as $FeSO_4$); 2) $FeSO_4$ to which large amounts of $KHSO_4$ have been added; 3) $FeSO_4$ to which large amounts of $ZnSO_4$ have been added. The mutual position of the curves along the abscissa is arbitrary.

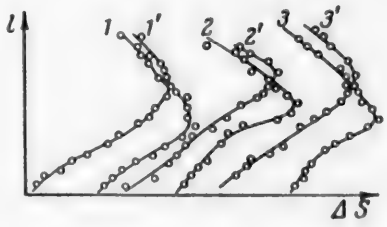

Fig. 4. The relationship between the character of the distribution of the blackening of iron lines and the presence of various anions in the plasma. 1) SO_4^{2-}; 2) Cl^-; 3) NO_3^-. The ordinary figures relate to the line Fe II 2598.4 while the dashed figure relate to Fe I 2719.02. The mutual position of the curves along the abscissa is arbitrary.

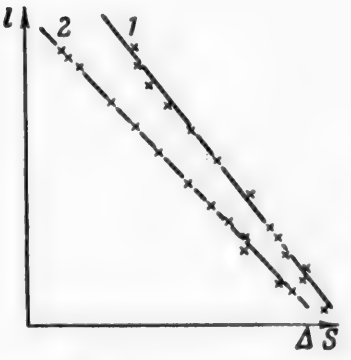

Fig. 5. The change in the difference in blackening of the fixed pair Fe II 2598.4 and Fe I 2719.02 (ΔS) along the length (l) of the plasma stream. 1) During excitation of the element from pure aqueous solutions; 2) on addition of a solution containing 50% ethanol.

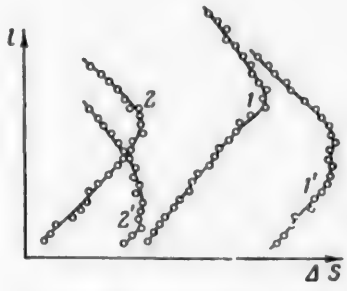

Fig. 6. Effect of addition of ethanol (50%) on the distribution of blackening of the iron lines Fe I 3020.6 (1) and Fe II 2392.0 (2) along the length of the plasma stream. The ordinary figures refer to solutions free from ethanol; the dashed figures refer to solutions which ethanol has been added. The relative position of the curves along the abscissa is arbitrary.

Technique for analyzing alloys. The technique described below can be used for the quantitative determination, in practice, of all the alloying elements usually added to titanium alloys (Al, Cr, Mo, Fe, Si, V, Mn, Sn). Nevertheless, in the present article the possibilities of the technique are described only with respect to the determination of five of these additives, the so-called α- and β-stabilizors – Al, Cr, Mo, V, and Mn – the content of which in various alloys can be varied over a wide range of 0.1 to 10%.

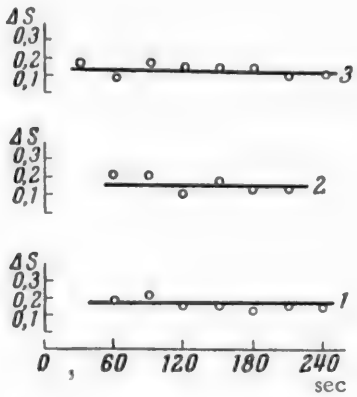

Fig. 7. The degree of constancy of the blackening of the analytical lines of various elements (ΔS) during their excitation from solution in a plasma stream. 1) For the lines Al I 3944.0; 2) Cr I 4254.3; 3) Fe I 3019. The blackening level of the line is arbitrary.

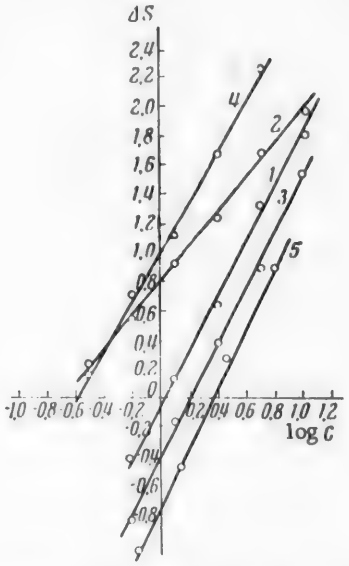

Fig. 8. Calibration curves for the determination of Al (1) Gr (2); Mo (3); Mn (4); and V (5) in titanium alloys.

TABLE 1. Analytical Lines of the Elements and Their Excitation Potentials

Lines of test elements		Lines of the reference element	
wavelength (A)	excitation energy, ev	wavelength (A)	excitation energy, ev
Al I 3944,0	3,14	Co I 3995,3	4,03
Cr I 4254,3	2,91	Co I 3995,3	4,03
V I 3183,4	3,91	Co I 3412,0	4,15
V I 4379,2	3,13	Co I 3995,3	4,03
Mo I 3170,3	3,91	Co I 3412,0	4,15
Mn I 2801,1	—	Co I 3412,0	4,15

TABLE 2. Results of Chemical (Ch) and Spectrographic (S) Analysis of Standard Alloys

Standard No.	Mo		Cr		Al		Mn	
	Ch	S	Ch	S	Ch	S	Ch	S
11	2,50	2,52	4,16	4,21	2,90	2,92	3,15	3,10
12	—	—	0,92	0,89	3,83	3,67	0,72	0,68
13	—	—	—	—	5,03	5,13	—	—
14	0,74	0,70	1,60	1,59	5,31	5,20	1,10	1,07
17	1,50	1,66	2,35	2,40	7,02	6,90	0,79	0,78

a) Preparation of standard solutions and preparation of samples for analysis. Standard solutions are prepared by mixing calculated amounts of solutions of the chlorides of the test elements and of the base element (titanium), with addition of 5 ml of a cobalt salt solution (10 mg Co/ml), cobalt being used as the reference element. A standard with the maximum content of the test components is first prepared, and the other standards prepared from this by appropriate dilution with a solution of titanium salt containing 1% Ti.

A 0.5 g aliquot of the turnings of the test alloy is placed in a chemical beaker, 20 ml of chemically pure concentrated hydrochloric acid which has been checked beforehand for the absence of the elements to be determined is added, the beaker is covered with a watch glass and the contents of the beaker are heated on a sand bath until the alloy has dissolved. As the solution is evaporated HCl is added to it in small portions. When dissolution is complete, the dark-violet colored solution of titanium trichloride is oxidized with chemically pure, concentrated nitric acid, the latter being added dropwise. The solution obtained is transferred to a 50 ml standard flask and 5 ml of a solution of a cobalt salt (10 mg Co/ml) added, the solution is made up to the mark with distilled water, and after thorough mixing it is analyzed.

b) Technique for the spectrographic determination of elements. Experience with a plasma generator [9] has shown that in order to increase the stability of the stream, it is expedient to increase the internal diameter of the outlet nozzle from 5 to 6.5 mm. Under such conditions the amount of cooling gas (argon) used proved to about 6.5 liters/min, while the optimum parameters of the glass spraryer which ensure the best operational conditions of the excitation source changed very little. The gas pressure at the sprayer inlet was 2.5 atm, while the amount of solution used was 6-8 ml/min. The distance between the electrodes was kept constant at 3 mm. Both carbon electrodes were changed after obtaining three successive spectra belonging to a standard or to a test sample. The generator was operated from a 20 amp dc arc at a voltage of 270 v. The standard solution or the test sample converted into an aerosol by the sprayer passed together with the cooling gas into the inner cavity of the generator, and thence into the plasma stream.

The analytical lines of the elements, and the position of the operating part of the plasma stream were chosen in accordance with the results of preliminary experiments (Fig. 1) so that determination of all the elements could be realized for one (unchanged for the various elements) position of the spectrograph slit relative to the chosen operating part of the plasma stream. The distance in this case was 22 mm. The operating part of the plasma stream located at this height was projected through a one lens illumination system onto the slit of an ISP-22 spectrograph.

The analytical lines used in this work and the excitation energies corresponding to them are given in Table 1.

The spectra were photographed on spectrographic plates type II with a sensitivity of 16 GOST units, and were developed in D-19 developer.

The preliminary exposure was 20 sec, while the main exposure was 75 sec. The spectrograms obtained after photographing the standard solutions and the alloy samples were measured photometrically on a MF-2 microphotometer. The extent of the stability of the photometer readings for some of the lines of the different elements is shown by the curves in Fig. 7. Calibration curves were constructed within the coordinates $\Delta S - \log c$. They are shown in Fig. 8. They are linear over a wide concentration range.

The mean arithmetic error for the reproducibility of spectrographic determination, calculated from three parallel measurements, varies within the limits 3-4%.

In order to check on the accuracy of analysis by the technique described, a group of standard alloys which had been reliably analyzed in seven chemical laboratories was used; these samples were kindly presented to us by K. A. Sukhenko to whom we should like to express our thanks. The mean results of the analyses of these samples which we carried out are compared with the results of chemical analyses in Table 2.

As is evident, the degree of agreement between the results obtained by the two methods can be regarded as completely satisfactory.

SUMMARY

A method has been developed for the quantitative spectrographic determination of impurities and alloying additions in titanium alloys using a plasma generator. The alloys are brought into solution in order to carry out the analyses. The mean arithmetic error of the reproducibility in three parallel determinations is 3-4% (relative). The deviation between the results obtained by this method and by chemical analysis is of the same order.

The excitation conditions of the spectra of various elements in this source have been studied systematically, and the effect of the ionization potentials of the elements, the excitation energy of the spectral lines, the source temperature, the presence in solution of organic materials, and the presence of cations and anions of other elements on these excitation conditions has been established.

Differences in the excitation conditions of the spectral lines of the elements in different zones of the plasma generator stream have been established.

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SEPARATION OF ALKALI METAL IONS AND ISOLATION OF MAGNESIUM IONS FROM THEM BY ELUANT CHROMATOGRAPHY

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 538-543,
September-October, 1961
Original article submitted July 15, 1960

Despite the successes achieved in the ion exchange chromatography of the alkali metals [1-3], there is still a number of important questions which demand further study.

In none of the published papers devoted to the study of the effect of such factors as the particle size of the ion exchange resin, the length of the ion exchange column, elution rate, and the ratio of the components of the synthetic mixtures, on the efficiency of separation, has consideration been given to the question of the criteria which should be followed in choosing an ion exchange resin which is suitable for carrying out eluant chromatography of the alkali metals. Apparently, no one has completely separated mixtures of all the alkali metals, while the most successful separation has only been effected by using not readily available ion exchange resins – Amberlite IR-100, Wofatite KS [4, 5] – or special resins Wofatite KPS-200 [6]. Good separation of mixtures of sodium and potassium has been achieved on KU-2 containing a high divinylbenzene content [7] and on colloidal Dowex-50 [8], but lithium was only separated from sodium and potassium on this resin with difficulty [9] by increasing its dispersivity sharply, a factor which complicates operation since it is necessary to create a vacuum in the lower part of the column. An even more difficult problem is separation of potassium–rubidium and rubidium–cesium mixtures, because of the very close values of the radius of the hydrated ions [10]. Apparently, only Kayas [4] has been successful in quantitatively separating potassium from rubidium; in the paper published earlier by Cohn and Cohn [11] this separation was not quantitative.*

Papers have been published on the separation of mixtures of lithium and magnesium [12], and also of mixtures of magnesium, sodium, and potassium [8], but separation of magnesium from a mixture of all the alkali metals has not been studied.

In the present article a description is given of a method which has been developed for the eluant chromatographic separation of mixtures of all five alkali metals, and also of mixtures of the alkali metals with magnesium, using readily available cation exchange resins–sulfonated polybutadiene resins. A study of the selectivity of the proton – alkali metal cation equilibrium exchange on these cation exchange resins and on KU-2 has enabled us to give some indications on the choice of cation exchange resin suitable for successfully separating mixtures of the alkali metals by eluant chromatography.

EXPERIMENTAL

The selectivity of the proton–cation equilibrium exchange. We studied the selectivity of the equilibrium exchange** on two polybutadiene cation exchange resins–sulfonated polybutadiene rubber (ion exchange resin SKB) and on a sulfonated polybutadiene vulcanizate containing 4% combined sulfur per 100 parts by weight of polymer (cation exchange resin SBR × 4) – and also on the cation exchange resin KU-2 containing 4 nominal percent divinylbenzene. The preparation and properties of the sulfonated polybutadiene have been described in [3]. The exchange capacity of SKB and SBR × 4 with respect to sodium chloride is 2.5 and 2.1 mg. equiv per g of dry resin respectively. For the study of equilibrium exchange carried out at room temperature and at an ionic strength of the equilibrium solution of 0.1, the technique described in the literature [14] was adopted. Since we worked with chlorides, the content of alkali metal in the equilibrium solution and in the resin phase was determined by Mohr's chloride method. The

* New possibilities of separating alkali metals which are opened up by the use of cation exchange resins containing weakly acid groups, e.g., the Russian phosphoric acid cation exchange resin RF, are pointed out in the review by M. M. Senyavin [1].

** A. N. Pokrovskaya and V. S. Soldatov carried out these experiments.

experimental results are shown in Figs. 1 and 2 as partition curves of the ions between the resin and equilibrium solution phases within the coordinates, equivalent fraction of the metal ion in the resin phase ($\bar{x}_M$) – equilibrium fraction of the ion in the equilibrium solution phase (x_M).

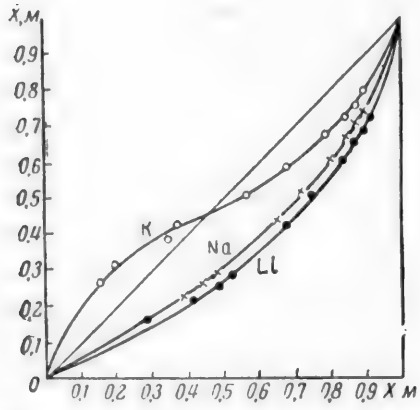

Fig. 1. Distribution of Li, Na, and K between SBR x 4 and solution (in all these diagrams the figure at the side of the symbol for the element denotes the number of mg. equiv. introduced.

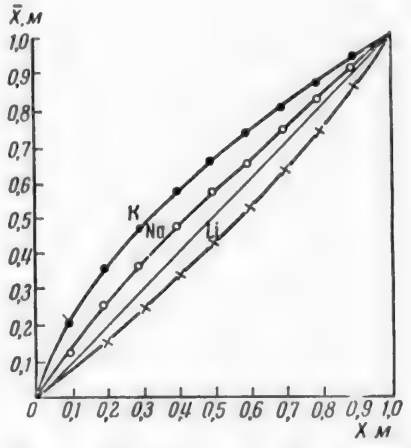

Fig. 2. Distribution of Li, Na, and K between KU-2 and solution.

Free Exchange Energy of the Proton–Cation Exchange in Infinitely Dilute Solutions

	Ion exchange resin SBR x 4		Ion exchange resin KU-2	
RM	K_{sol}	$-\Delta F$, cal/g. equiv.	K_{sol}	$-\Delta F$, cal/g. equiv.
RLi	5.0	943	1.5	237
RNa	3.3	699	0.9	−62
RK	2.0	406	0.6	−300

It is clear from the figures that on the resin SBR x 4 (SKB behaves in a similar fashion) the partition curves of the ions between the phases (with the exception of potassium in dilute solutions) lie below the diagonal of the square $\bar{x}_M - x_M$, i.e., the selectivity coefficient of the proton–cation equilibrium exchange which is equal to the ratio of the equivalent fractions of hydrogen ions and metal ions in the resin phase divided by the same ratio in the equilibrium solution phase [15] is greater than unity.* On the cation exchange resin KU-2, as is evident from Fig. 2, the selectivity coefficient during the exchange of lithium for protons is greater than unity throughout the whole range of compositions, while for the exchange of sodium and potassium for protons it is less than unity.

The values of the partition coefficients of hydrogen ions for the cation exchange resins SBR x 4 and KU-2 in the corresponding metal forms are given in the table, they are equal to the tangents of the slopes of the partition coefficients at $x_M = 1$. The same table contains the values of the maximum work of transferring a g. equiv of hydrogen ions from an infinitely dilute solution into the ion exchange resin in the metal form; these values are expressed in calories per g. equiv. and are calculated by means of the equation:

$$A = -\Delta F = RT \ln K_p.$$

It is clear from the results given in the table that the ratio of the partition coefficients in both resins is approximately the same for this series of ions. However, in the case of the resin SBR x 4 (and also in the case of SKB) the transfer of hydrogen ions from an infinitely dilute solution into the metallic form of the resin is a spontaneous process, while in the case of KU-2 this process is only spontaneous for the resin in the lithium form.

* S-shaped partition curves similar to the curve for potassium in Fig. 1 can be obtained on cation exchange resins containing different types of functional groups [16]. The polyfunctionality of sulfonated polybutadienes has been established in [13].

This is an important factor for realizing eluant chromatography. In fact, since the elution process proceeds spontaneously on sulfonate polybutadiene resins even in infinitely dilute solutions of acids, the choice of an eluant when using resins of this type is a relatively simple operation; it is necessary to start elution with very dilute acid solutions and then by gradually increasing the acid concentration it is possible to obtain constricted but not overlapping zones for the individual ions.

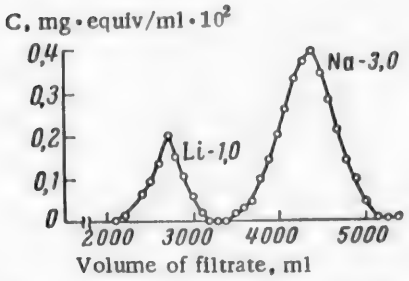

Fig. 3. Separation of Li and Na on KU-2.

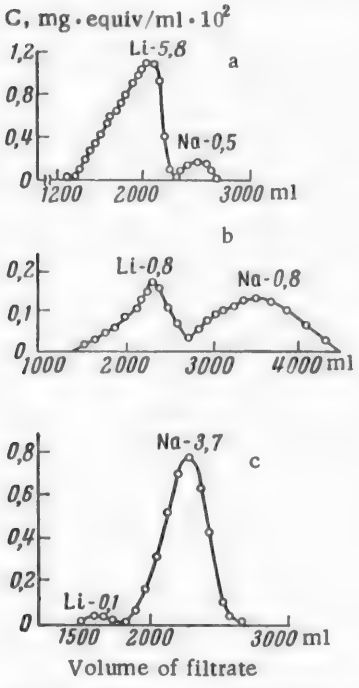

Fig. 4. Separation of mixtures of Li and Na on SBR × 4. a) Li : Na = 11,6 : : 1; b) Li : Na = 1 : 1; c) Li : Na = 1 : 37.

For separation of alkali metal cations (with the exception of lithium) on the cation exchange resin KU-2 there is no point in starting a search for eluants with very dilute solutions of acids, while it is necessary to find empirically, or by calculation by means of the isotherms of the chemical reactions, that acid concentration (naturally this will have a particular value for each of the ions in a mixture) at which the hydrogen–cation exchange will become a spontaneous process.* This fact transforms the empirical choice of eluants for ion exchange resins of the KU-2 type into a vague problem, and even under the best conditions into a very difficult operation.

In agreement with the considerations outlined above, it has been found possible to separate sodium and potassium ions on Dowex-50 by means of fairly concentrated acid – 0.7 N HCl [8], while attempts to separate a ternary mixture of lithium–sodium–potassium with the same eluant proved to be very difficult, as noted already. From a thermodynamic point of view such an attempt is unfounded, since at such a hydrogen ion concentration, the exchange process is spontaneous for all three cations. As is obvious from the results given in the table for KU-2, separation of mixtures of lithium and sodium should be carried out with acid whose concentration is such that the hydrogen–sodium exchange has not yet become a sharply spontaneous process. These ideas have been confirmed experimentally. We were able to separate, without any difficulty, mixtures of lithium and sodium on KU-2 containing 4% divinylbenzene and consisting of coarsely dispersed spherical particles with a particle size of 0.25-0.50 mm in a column of 1 × 100 cm, using 0.05 N HCl at the rate of 3 ml per minute. The results of one of these experiments,** in which a mixture containing 1 mg. equiv. of lithium and 3 mg. equiv. of lithium was separated, are shown in Fig. 3.

A characteristic feature is that the most successful experiments in separating mixtures of the alkali metals have been carried out by means of dilute acids. Thus Kayas [4] used 0.1 N HCl on Amberlite IR-100, Wickbold [5] used 0.1 N HCl on Wofatite KS, while Jentzsch and Frotscher [6] used 0.01 N HCl on Wofatites KPS-200 and F. There is a basis for assuming that the resins mentioned are characterized, like the sulfonated polybutadiene resins, by the fact that the hydrogen–cation exchange proceeds spontaneously on them from infinitely dilute solutions of acids.

Thus in order to separate mixtures of ions successfully by eluant chromatography, on the basis of an empirical choice of the hydrogen ion concentration of the eluants, it is extremely important that in addition to marked differences in the values of the selectivity coefficients of the hydrogen–cation exchange equilibrium, this exchange should be spontaneous in the region of infinitely dilute solutions of hydrogen ions.

Experiments on chromatographic separation. In order to obtain results comparable to those given in the literature, the experiments on chromatographic separation were carried out under conditions analogous to those used by Wickbold [5] and Jentzsch and Frotscher [6]. The column whose dimensions were 1 × 100 cm, contained 56-59 g of ion exchange resin with particle size 0.1-0.25 mm. The elution rate was 5 ml per minute. In Fig. 4 are shown elution curves obtained during the separation of mixtures of lithium and sodium in various proportions, 0.025 N HCl being used as the eluant.

* It is necessary, however, in order to carry out these calculations, to have data on the activity coefficients of the components.

** Carried out by N. A. Polyak.

It is clear from the diagram (curve "c") that the separation is still quite clear cut when the lithium content is less than 3% of the mixture. Separation of mixtures of sodium and potassium is even better. In Wickbold's paper [5] sodium and potassium gave a mixed zone when their contents in the mixtures were in the proportion 1 : 9.

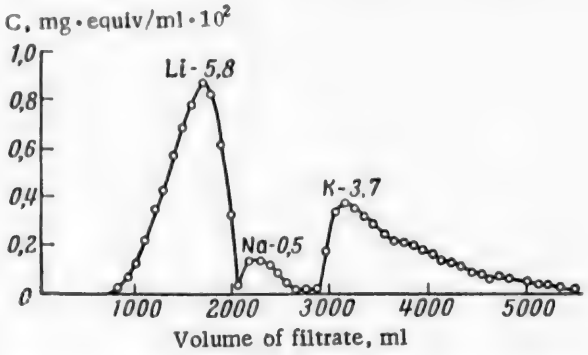

Fig. 5. Separation of mixtures of Li, Na, and K on SBR x 4.

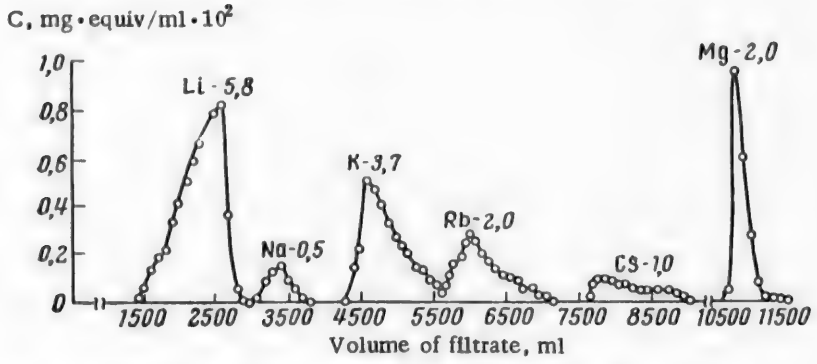

Fig. 6. Separation of mixtures of Li, Na, K, Rb, Cs, and Mg on CBR x 4.

Figure 5 shows the results obtained during separation of lithium, sodium, and potassium by means of 0.025 N HCl passed through the column at a rate of 5 ml/minute, when the relative loading of the column was 0.1.

The clearness of the separation is approximately the same as that obtained in [5]; the lithium and sodium zones almost touch each other, while there is a considerable gap, amounting to about 200 ml in our experiments, between the sodium and potassium zones.

During separation of a mixture of all five alkali metals, sodium and lithium were eluted with 0.025 N HCl, while rubidium was eluted with 0.05 N HCl, and cesium with 1.0 N HCl. During separation of the given component mixture the elution rate had to be dropped to 2 ml/min, since at higher elution rates potassium and rubidium gave a small mixed zone.

We established during the course of a large number of experiments that separation is most clear cut on the cation exchange resin SKB: there is an appreciable gap between the lithium and sodium zones, while the sharpness with which potassium and rubidium are separated also increases. Comparison of the results of experiments carried out on SKB with the results given in [5] and [6] shows that the partitioning capacity of SKB is slightly greater than that of Wofatite KS, and considerably higher than that of Wofatite F, and is only inferior to Wofatite KPS-200. A slight drawback of sulfonated polybutdiene resins is the necessity of using comparatively large volumes of eluent during elution of the alkali metals from the column. However, when working with small amounts of components in the mixtures (of the order of some tenths of a mg. equiv.), and particularly when using automatic collectors, this drawback is unimportant.

Compared with other divalent cations, it is known that [9] magnesium is the most difficult element to separate from the alkali metals by ion exchange chromatography. Mixtures of all the alkali metals and magnesium were separated very well on the sulfonated polybutadiene resins studied in the present work.

Elution curves for a mixture of all the alkali metals and magnesium are shown in Fig. 6. Lithium and sodium were eluted with 0.025 N HCl, potassium with 0.05 N HCl, rubidium with 0.085 N HCl, cesium with 0.1 N HCl, and magnesium with 0.5 N HCl.

SUMMARY

A study has been made of the selectivity of the proton–alkali metal cation exchange equilibrium on sulfonated polybutadiene (SKB), on sulfonated polybutadiene vulcanizate containing 4% combined sulfur (SBR × 4), and on KU-2 containing 4% divinylbenzene. The free energies of the proton–cation exchange in infinitely dilute solutions of hydrogen ions have been calculated. It has been shown that the sign of the free energy of the proton–cation exchange is important for a rational selection of eluants.

The readily available sulfonated polybutadienes – SKB and SBR × 4 are quite suitable for the quantitative separation of mixtures of the ions of all five alkali metals, and also for the separation of these ions from magnesium by eluent chromatography.

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DETERMINATION OF SMALL AMOUNTS OF POTASSIUM BY AN ISOTOPE DILUTION METHOD

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 544-548, September-October, 1961
Original article submitted August 8, 1960

There are no satisfactory methods at present for the determination of about 0.001 g of potassium in one g of rocks and minerals with an accuracy of down to 2-3%. In order to determine the absolute age of a specimen, development of techniques for the determination of small amounts of potassium is of great practical importance. A solution of this problem would allow one to determine age by the argon method on the basis of primary rocks with a potassium content of less than 1%. The use of the isotope dilution technique would appear to be the most promising approach. Using such a technique it should be possible to achieve a considerably higher sensitivity and accuracy than is possible by ordinary chemical methods. We set ourselves the problem of developing a method for the determination of potassium by means of the MI-1305 mass-spectrometer, and comparing the results obtained with the results of chemical determinations. We chose samples with a low potassium content for study: diabases, beryls, and tourmalines. The diabases were decomposed by the usual method [1]. The difficulties involved in decomposing beryls and tourmalines led us to use a special chemical method for their treatment.

Technique for the chemical analysis of beryls and tourmalines. On clinkering tourmalines and beryls by the classical Lawrence–Smith method an appreciable part of the sample remains undecomposed. We tried to determine potassium quantitatively in beryls and tourmalines after using Yashchenko and Barshavskii's rapid method [1]. For determining potassium by this method micas are decomposed with a mixture of hydrofluoric and oxalic acids. Beryls and tourmalines, however, are not completely decomposed by this method. On the basis of the work of Tananaev and Smyshlyaev [2], the authors, on Yashchenko's advice, have modified this method. Decomposition with the mixture of hydrofluoric and oxalic acids was replaced by sintering of the minerals with ammonium fluoride, and subsequent decomposition of the fluorides with oxalic acid. Ammonium fluoride is a more active reagent. During decomposition of the minerals, in order to make the analysis quantitative, the samples must be given repeated treatment with ammonium fluoride. Decomposition of the fluorides and silicofluorides formed with oxalic acid, and the subsequent analytical procedure were carried out in the same way as in the method published earlier [1]. The complete analytical procedure which we followed is given below.

The test samples were ground as carefully as possible, since completeness of decomposition depends on the degree of grinding. A 1 g aliquot was placed in a platinum basin and mixed with ten times its amount of ammonium fluoride. The basin was placed on a flask heater, and sintered at 300-400°. Ammonium fluoride reacts vigorously over this temperature range with silicate powder, and the sample is decomposed in a matter of a few minutes. A further 2-3 g of NH_4F was added to the fluorides formed and sintering repeated. Six-seven g of oxalic acid was added to the dry residue; this was followed by addition of hot water, and the contents of the basin evaporated on a water bath to dryness. The dry residue was again moistened with hot water and the evaporation repeated. The platinum basin was then transferred onto a sand bath, where the oxalic acid fused and started to decompose. Oxalic acid was finally removed and decomposed on a flask heater at 250°.

Hot water was added to the dry residue, and 5-6 ml of concentrated HNO_3 and 8-10 ml of $HClO_4$ added. The basin was placed on a water bath and evaporated until perchloric acid fumes started to come off; it was then placed on a sand bath on which the residue was evaporated to a moist state. On cooling the basin, the mass was extracted. A slight excess of perchloric acid is necessary for preventing formation of basic salts.

The residue was dissolved in hot water, transferred to a beaker, and boiled for 2-3 min. Traces of silica, and other insoluble acids which may be present (titanic, niobic, tantalic acids etc.) were filtered off. A further 5-6 ml of $HClO_4$ was added to the solution in order to ensure complete removal of nitric acid and to obtain pure perchlorates.

The solution was again evaporated in succession on a water bath and on a sand bath to the moist salt stage, the salts were treated with a few 25-30 ml portions of ethanol (rectified) containing $HClO_4$ (400 ml of C_2H_5OH + 2 ml of 40% $HClO_4$). The ethanol solution of the perchlorates was poured off through a filter. The total volume of ethanol was about 100 ml. The residue consisting in the main of $KClO_4$, in the beaker and on the filter, was dissolved in hot water, 0.05-1.0 ml of $HClO_4$ was added to the solution, and the solution again evaporated to the moist salt state, the salts were again treated 6-8 times with absolute ethanol containing $HClO_4$, smaller portions of the ethanol solution being used this time. The $KClO_4$ precipitate was dissolved in water and transferred to a small tared platinum basin. The solution was evaporated to dryness on a water bath. Potassium perchlorate was finally dried for 30 min in an oven at 350° and weighed. The conversion factor to potassium is 0.2822. A complete analysis takes 10-12 hr.

Isotope dilution method. Potassium enriched with K^{41} to the extent of about 100 times was used as the stable indicator. The amount of potassium m_0 in the test sample is found by means of the formula:

$$m_o = m_n \cdot \frac{M_o}{M_n} \cdot \frac{n_c - n_n}{n_o - n_c} \cdot \frac{1 + n_o}{1 + n_n}, \qquad (1)$$

where m_n is the amount of indicator with a ratio of the isotopes $K^{39}/K^{41} = n_n$, n_0 is the ratio of K^{39}/K^{41} in the sample n_c is the same ratio for the mixture, M_0 and M_n is the atomic weight of potassium in the sample and in the indicator.

In order to determine potassium with a relative error of about 3% the values of the ratios of the isotopes should be known to an accuracy of down to 1%. Published results on the isotopic composition of reagent and natural potassium are contradictory.

According to results given by various authors, the value of K^{39}/K^{41} changed in the samples tested from 12.6 to 14.6 [3-14].

However, as shown in [13] and [14], the scatter of the results is not caused by the natural fractionation of the isotopes. Various research workers have used different ion sources for ionizing the potassium: 1) a ribbon ionizer with a very thin layers of potassium salts or oxide amounting to $\leq 10^{-6}$ g; 2) a ribbon with a dense solid or fused salt, or with oxide, amounting to $n \cdot 10^{-4}$ g; 3) a pure or oxidized metal surface saturated with potassium; 4) metallic potassium or its oxide as vapor.

In the case of a source of type 1, the value of K^{39}/K^{41} changes according to a law similar to the law of molecular diffusion of a gas through an aperture into a vacuum. Discrimination according to the masses corresponding to the value $\sqrt{39/41}$ occurs. The measured ratio K^{39}/K^{41} decreases with time during an experiment.

When using ionic sources types 2 and 3 the main role is played by diffusion inside the melt or crystalline lattice. When $> 10^{-3}$ g potassium is placed on the ribbon, the ratio K^{39}/K^{41} changes regularly with time up to the point at which an equilibrium state is reached [10, 13, 14]. On placing $10^{-5} - 10^{-4}$ g of pure potassium salt on the ribbon it was found that the change in the ratio K^{39}/K^{41} during an experiment is less than 1%. We took this into account when placing the sample on the ribbon.

Measurements were made on the standard MI-1305 mass-spectrometer. A single beam method of measurement was adopted. Surface ionization on tungsten was used. Tungsten ribbons, as was established, contain a relatively large amount of potassium which gives rise to a "background" to the 39 and 41 masses. In order to purify the ribbons they were calcined beforehand for 2-3 hr outside the mass-spectrometer at 1450° in a vacuum of about 10^{-5} mm Hg.

Before each experiment the ion source was carefully washed in 2% HCl solution, distilled water, and ethanol. As a rule, after calcining the ribbons and washing them, the background did not exceed 0.1% of the values of the K^{39} and K^{41} peaks. A few drops of the test solution of K_2SO_4 was then placed on a tungsten ribbon. The ribbon was dried under an infrared lamp, after which the ion source was placed in the mass-spectrometer. About $5 \cdot 10^{-5}$ g of potassium is required for an analysis. Thirty-fifty measurements of the ratios of the K^{39} and K^{41} isotopes were made in each experiment.

Determinations of the ratio K^{39}/K^{41} in potassium from reagents were also made, an oven ion source and ionization with electrons being used. A value of 13.95 was obtained. This does not differ appreciably from the result found on using the surface ionization method (Table 1).

It is clear from Table 1, that the isotopic composition of potassium was identical in all the natural samples we measured, and coincided with the isotopic composition of reagent potassium: $K^{39}/K^{41} = 13.92 + 0.09$. This value does not differ from that of Reutersward which he obtained under similar measurement conditions $-13.88 + 0.07$ [13].

An indicator solution ($K^{41}Cl$) of known concentration was prepared for quantitative determination. For this purpose a subsidiary solution of reagent K_2SO_4 was prepared. It was standardized gravimetrically; aliquots of the solution were accurately weighed out, evaporated to dryness, and the weight of dry salt determined.

Weighed volumes of the subsidiary solution and the indicator potassium solution were then mixed. From the measured katio K^{39}/K^{41} in the mixed solution it was possible to calculate the titer of the solution of the indicator potassium solution.

TABLE 1

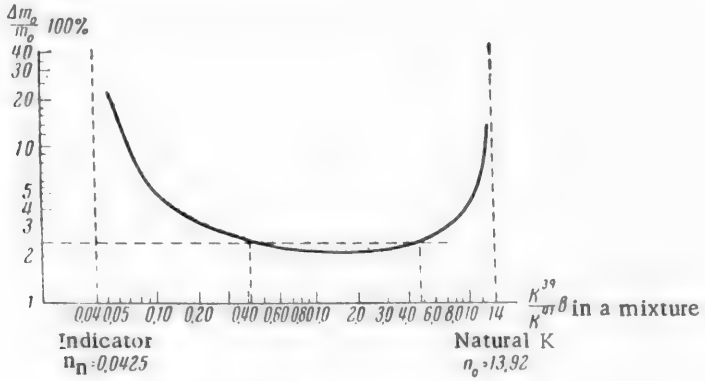
Sample	K^{39}/K^{41}	Sample	K^{39}/K^{41}
Reagent K_2SO_4	13.92 ± 0.09	Beryl B	13.84 ± 0.10
Reagent KCl		Tourmaline A	13.80 ± 0.08
(Oven source)	13.95 ± 0.07	Beryl K-300	13.80 ± 0.10
Beryl 993	14.10 ± 0.10	Muscovite K-300	13.77 ± 0.08

The procedure adopted for the isotope dilution technique was as follows: decomposition of an aliquot with ammonium fluoride was carried out as indicated above. An accurately weighed amount of the indicator solution was added to the basin containing the sinter.

For establishing the amount of indicator solution that should be added, the following fact should be borne in mind. The error in determining the amount of potassium in a sample is given by the expression (obtained as usual from formula 1):

$$\frac{\Delta m_0}{m_0} \approx \frac{\Delta T_n}{T_n} + \frac{\Delta B_n}{B_n} + \frac{(n_0 - n_n)\cdot \Delta n_c}{(n_c - n_n)\cdot(n_0 - n_c)} + \frac{(1 + n_c)\,\Delta n_n}{(n_c - n_n)\cdot(1 + n_n)} + \frac{(2n_0 - n_c + 1)\cdot \Delta n_0}{(n_0 - n_c)\cdot(1 + n_0)}, \qquad (2)$$

where T_n is the titer of the indicator, B_n is the weight of indicator solution taken. The value of $\Delta B_n/B_n$ is much less than the sum of the remaining terms on the right hand side of expression 2. Variations in the error in weighing the indicator solution, for different value of B_n, do not affect the total error Δm. Accordingly, for a given indicator with a titer T_n and under conditions such that n_0 = const an n_n = const the error in determining potassium is only a function of one term n_c. The function $\Delta m/m_0 = F(n_c)$ which we calculated is shown graphically in the diagram. Analysis of this curve shows that the minimum error in determining potassium is observed under conditions for which the ratio of the isotopes K^{39} and K^{41} in a mixture is near 1 (n_c about 1). For the range $0.4 \leq n_c \leq 5$, the error does not exceed ± 2.5%. Starting with a natural sample, one can get a rough (with an accuracy of an order) idea of its expected potassium content, and thereby take a suitable amount of indicator solution so that the condition $0.4 \leq n_c \leq 5$ is obeyed. After adding the indicator to the basin, oxalic acid was added. The subsequent procedure was the same as that described above, the only difference being that the yield of potassium may be less than 100%.



The relationship between the error in determining potassium and the ratio K^{39}/K^{41}.

The perchlorates obtained during the final analytical stage were converted to the sulfates in the platinum basin. The sulfuric acid was carefully removed by heating. A few drops of water when then added to the contents of the basin. The solution was placed on the ribbon of the ion source by means of a capillary.

The reproducibility of the experimental results obtained by the isotope dilution method are illustrated in Table 2.

TABLE 2.

Sample (weight 1 g)	Amt. of indicator solution added, g	K^{39}/K^{41}	K, %	K_{mean}, %	Error, %
Diabase № 2062	0,9228	3,31	0,294	0,294±0,001	±0,3
» № 2062	0,8526	3,59	0,295		
» № 2177	0,7148	3,34	0,226	0,224±0,002	±0,9
» № 2177	0,7002	3,37	0,222		
» № 2101	0,6508	3,83	0,257	0,255±0,002	±0,8
» № 2101	0,9460	2,90	0,253		
» № 2247	0,6480	2,17	0,116	0,114±0,002	±1,8
» № 2247	0,8744	1,64	0,112		
» № 2247	0,7082	1,86	0,115		
» № 2159	0,8404	3,85	0,319		
» № 2159	0,5954	2,92	0,339	0,329 ±0,007	±2,1
» № 2159	1,221	2,80	0,329		
Tourmaline A	1,2481	2,31	0,237	0,242±0,005	±2,1
» »	1,5990	1,94	0,247		
Beryl K-300	1,1014	1,56	0,117	0,116±0,001	±0,9
	1,0216	1,63	0,114		

TABLE 3

Sample	K found, %		
	by the perchlorate method		mass-spectrometric method
	decomposition with $HF + H_2C_2O_4$	decomposition with with $NH_4F + H_2C_2O_4$	
Diabase № 2177	0,26±0,02		0,224±0,002
» № 2101	0,23±0,02		0,255±0,002
» № 2247	0,11±0,02		0,114±0,002
» № 2159	0,31±0,02		0,329±0,007
Tourmaline A		0,20±0,02	0,242±0,005
» 1551		0,21±0,02	0,218±0,004
Beryl K-300		0,09±0,02	0,116±0,001
» № 993		0,15±0,02	0,145±0,003
» B		0,22±0,02	0,206±0,006

The potassium contents given in Table 2 have been corrected for the amount of potassium in the reagents. In the case of diabases the correction was about 1% of the potassium content, while for beryls and tourmalines it amounted up to 15%.

Results of the determination of potassium in minerals by two methods – chemical and mass-spectrometric – are compared in Table 3.

The slight scatter in the results obtained by the two methods can be explained by the insufficient accuracy of the chemical method at low potassium contents in the minerals. It is obvious that the results obtained by the isotope dilution method are more reliable.

Potassium was also determined by isotope dilution in mica with a known potassium content. Chemical and mass-spectrometric determinations gave results in satisfactory agreement with each other.

In muscovite K = 300, the amount of potassium determined chemically was 8.28 and 8.30%, while by the mass-spectrometric method the value found was 8.13 and 8.36%.

In conclusion we should like to thank E. K. Gerling and M. L. Yashchenko for their continued interest and their help in the work.

SUMMARY

A method used for the quantitative chemical decomposition of tourmalines and beryls which are difficult to breakdown has been improved; the improved method ensures complete separation of potassium for analysis.

It has been shown that a mass-spectrometric method is suitable for the quantitative determination of potassium in minerals at a potassium concentration in the latter of less than 1%.

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GRAVIMETRIC DETERMINATION OF SCANDIUM WITH PHENYLPHOSPHINIC ACID

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 549-551, September-October, 1961
Original article submitted May 12, 1960

Scandium has a clearly expressed affinity toward phosphate ions. It forms sparingly soluble compounds with different phosphoric acid derivatives. Vickery's work [1] which involved the use of the radioactive isotope Sc^{46}, has shown that of all phosphoric acid derivatives, only disodium and phosphates and phytin precipitate scandium quantitatively. Vickery has also shown that scandium is not precipitated quantitatively as its hydroxide, oxalate, carbonate, or fluoride. Sodium pyrophosphate suggested by Beck [2], and subsequently studied in detail by Petru [3], does not give satisfactory results, since the precipitate partially dissolves in excess of reagent, and hydrolyzes during washing. Organic derivatives of pyrophosphoric acid, such as phytin, salts of the ester of aneurinepyrophosphoric acid and adenyltriphosphoric acid [4] form very sparingly soluble neutral salts with scandium. When precipitation is carried out with the reagents indicated, gravimetric forms are not obtained; these reagents are only used for separating and detecting scandium.

Recently, Bomberger [5] suggested hypophosphoric acid for the quantitative isolation and gravimetric determination of scandium. Materials which oxidize hypophosphoric acid, particularly nitrate ions, interfere.

Phenylphosphinic acid, the reagent which we should like to suggest, permits scandium to be precipitated quantitatively, while the precipitates obtained can be weighed after they have been dried at 120°.

TABLE 1. Composition of the Precipitate of Scandium Phenylphosphinate

$Sc_2(C_6H_5PO_2)_3 \cdot 3H_2O$	Content, %			$Sc_2(C_6H_5PO_2)_3 \cdot 3H_2O$	Content, %		
	calc.	by chemical analysis	by thermogravimetric analysis		calc.	by chemical analysis	by thermogravimetric analysis
C	35,29	34,5	35,6	H	3,44	3,7	
P	15,18	15,1		O	31,36		
Sc	14,73	14,5		H_2O	8,82		8,9

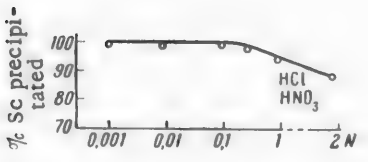

Fig. 1. Completeness of precipitation of scandium as a function of acid concentration.

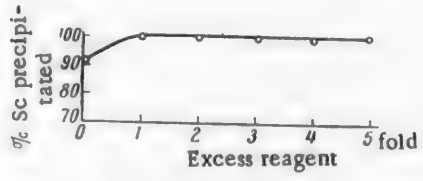

Fig. 2. Effect of excess reagent on precipitation of scandium.

Phenylphosphinic acid $C_6H_5PO(OH)_2$ reacts with scandium in an acid medium to form a white amorphous precipitate, which is soluble in dilute sulfuric acid, concentrated nitric and hydrochloric acids, and also in a saturated oxalic acid solution. Phenylphosphinic acid gives a visible turbidity at a scandium concentration as low as 15 μg Sc/ml.

The solubility of scandium phenylphosphinate is less than that of scandium phytate, and is equal to 10^{-7} M. A photometric method with xylenol orange was used for determining the solubility of the precipitate in water.

The composition of the air-dry precipitate os candium phenylphosphinate was established by thermogravimetric and chemical analysis (Table 1). The thermogram shows that the water is combined in a stoichiometric proportion in the precipitate of scandium phenylphosphinate, while it also shows that the weight of the precipitate remains constant over the range 140-240°, the precipitate starts to decompose at 250°; $Sc(HPO_4)_3$ is formed at 900°.

The fact that the composition of the precipitate remains constant, and the fact that the precipitate readily looses its water of crystallization at 120-160° mean that $Sc_2(C_6H_5PO_3)_3$ can be weighed directly (conversion factor 0.1616).

TABLE 2. Precipitation of Scandium with Phenylphosphinic Acid

Sc, mg		Error, mg	Media
taken	found		
5,91	5,90	—0,01	0.1 N HCl or HNO_3
7,24	7,20	—0,04	
11,82	11,78	—0,04	
5,91	5,88	—0,03	0.1 N HCl and a 2% solution of tartaric acid
7,24	7,22	—0,02	
11,82	11,79	—0,03	
2,95	2,89	—0,06	0.1 N HCl and a 2% solution of citric acid
5,91	5,90	—0,01	
7,24	7,20	—0,04	

TABLE 3. Determination of Scandium in the Presence of the Rare Earths

Ratio Sc: rare earths	Sc, mg		Error, mg	Ratio Sc: rare earths	Sc, mg		Error, mg
	taken	found			taken	found	
1 : 10	5,91	5,94	+0,03	1 : 100	2,95	3,04	+0,09
	7,24	7,30	+0,06		5,94	5,94	0,00
	11,82	11,82	0,00		7,24	7,23	—0,01

In order to establish the optimum conditions for precipitating scandium with phenylphosphinic acid we investigated the effect of the concentration of various mineral acids. For this purpose various amounts of hydrochloric or nitric acid were added to a standard hydrochloric acid solution of a scandium salt, the solution was diluted to 50 ml and heated almost to the boil, and scandium was then precipitated with a 1% solution of phenylphosphinic acid. Solution plus precipitate were kept on a water bath for 15-20 min, and the precipitate filtered off through a No. 4 filter crucible, and washed with a hot 1% ammonium nitrate solution and then with ethanol. The precipitate was dried at 120-140° and weighed as $Sc_2(C_6H_5PO_3)_3$. On the basis of the results obtained (Fig. 1), it was established that precipitation should be carried out from 0.1 N hydrochloric or nitric acid. At lower acidities scandium is still precipitated quantitatively, but precipitates of variable composition are formed. This is explained by the tendency of the scandium ion to hydrolyze and to form polymeric ions [6]. In the precipitates obtained at pH 4 and pH 1, the ratio of Sc to P is 2:2.4 and 2:3 respectively. Completeness of scandium precipitation was controlled by spectrographic analysis of the filtrates. Scandium phenylphosphinate does not dissolve in the presence of excess reagent; it is sufficient to take a twofold excess of reagent for quantitative precipitation of scandium (Fig. 2). Tartrates and citrates do not interfere with precipitation (Table 2).

On precipitating scandium in the presence of large amounts of the rare earths high results were obtained as a result of the coprecipitation of the latter, despite the fact that the rare earths are not precipitated by phenylphosphinic acid from 0.1 N hydrochloric acid solutions. Tartaric and citric acids prevent coprecipitation of the rare earths.

Scandium was precipitated as follows in the presence of the rare earths. Tartaric (or citric) acid was added to the test solution in such amount that its concentration in the final solution was 2%, hydrochloric acid was then added

until the pH was 1, the solution was diluted to 50 ml and was heated almost to the boil when the scandium was precipitated with a 1% solution of phenylphosphinic acid. The results obtained are given in Table 3.

The alkali and alkaline earth elements, zinc, nickel, cobalt, cadmium, and copper do not interfere with sandium determination. Elements such as zirconium, thorium [7], niobium, tantalum, hafnium, and titanium are precipitated together with scandium from strongly acid solutions.

In the presence of oxalate ions, when the stable anions $[Sc(C_2O_4)_3]^{3-}$ are formed, phenylphosphinic acid does not precipitate scandium, it does, however, precipitate zirconium, but not quantitatively.

SUMMARY

Phenylphosphinic acid, which forms a precipitate having the composition $Sc_2(C_6H_5PO_3)_3 \cdot 3H_2O$ with scandium, is suggested for the determination of the latter. The form in which it is weighed $Sc_2(C_6H_5PO_3)_3$ is obtained after drying the precipitate at 120-160°. In the presence of tartaric or citric acid, phenylphosphinic acid can be used for separating scandium from the rare earths.

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POTENTIOMETRIC DETERMINATION OF TRIVALENT THALLIUM WITH DIVALENT VANADIUM

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 552-554,
September-October, 1961
Original article submitted June 30, 1960

Solutions of divalent vanadium salts can be used for the potentiometric determination of a series of cations [1]. On the basis of the values of the normal potentials $V^{3+}/V^{2+} = -0.20$ v and $Tl^{3+}/Tl^{+} = +1.22$ v, one can assume that trivalent thallium should be reduced by solution of divalent vanadium salts. The present article is devoted to the results obtained during a study of the stoichiometric ratios during the interaction of trivalent thallium and divalent vanadium, while the possibility is demonstrated of using the latter for the quantitative determination of thallium.

EXPERIMENTAL

A VCl_2 (or VSO_4) solution was prepared by reducing ammonium vanadate with amalgamated zinc. An acid solution of a divalent vanadium salt keeps its titer for more than 20 days in the apparatus described by Busev and Li Gyn [2]. The VCl_2 solution was standardized potentiometrically against bismuth oxide. A solution of a trivalent thallium salt was prepared by dissolving a known amount of thallous acetate in water and acidifying the solution with sulfuric acid. The univalent thallium was oxidized with free chlorine, excess of which was removed by boiling. The solution obtained was diluted with water in a standard flask, and its concentration determined by means of diantipyrylmethane [3].

Potentiometric titration was carried out on a P-4 potentiometer, the reference electrode was a saturated calomel electrode, while the indicator electrode was a platinum wire. During thallium determination the vanadium solution was added from a microburet with scale divisions of 0.02 ml.

As experiment showed, trivalent thallium oxidizes divalent vanadium to the trivalent state. During potentiometric titration of a known volume of a trivalent thallium salt solution with a solution of divalent vanadium chloride or sulfate in a CO_2 atmosphere, at room temperature, a sharp potential jump (up to 600 mv) is observed at the end point. Satisfactory results were obtained on titrating solutions of trivalent thallium salt with 0.05 N VCl_2 in a medium of 6-10 N hydrochloric or sulfuric acid (Table 1).

On the basis of the results obtained the following potentiometric method has been developed for the determination of trivalent thallium.

Concentrated HCl or H_2SO_4 is added to a solution containing a trivalent thallium salt until the acid concentration is 6-10 N; CO_2 is bubbled through the solution which is titrated with 0.05 N VCl_2 solution until the platinum electrode gives a potential jump. Large amounts of Cd, Zn, and Pb (Table 2) do not interfere with determination of thallium. Precipitation of $PbCl_2$ does not interfere with titration. Fe^{3+} and Cu^{2+} ions, and oxidizing agents (MnO_4^-, $Cr_2O_7^{2-}$, $S_2O_8^{2-}$ etc.) interfere.

Determination of thallium in bricketted cadmium. An aliquot of cadmium (1.0-1.5 g) is dissolved in 10 ml of 2 N H_2SO_4 and 1 ml of concentrated HNO_3. The solution is heated on a sand bath until the nitrogen oxides have been removed, and the univalent thallium is oxidized with chlorine or ammonium persulfate. Excess oxidizing agent is removed by heating, HCl, or H_2SO_4 is added until the requisite acid concentration is obtained, and the solution titrated potentiometrically with 0.05 N VCl_2 solution.

Determination of thallium in slag. An aliquot of slag is dissolved in 10-15 ml of 0.5 N HNO_3, the thallium is oxidized to its trivalent state in which it is titrated with VCl_2 solution.

In order to check on the accuracy of the results obtained, after the end point had been reached a known amount of a standard solution of trivalent thallium was added and titration continued. Results of such determinations are given in Table 3.

TABLE 1. Potentiometric Determination of Trivalent Thallium with VCl_2 Solution

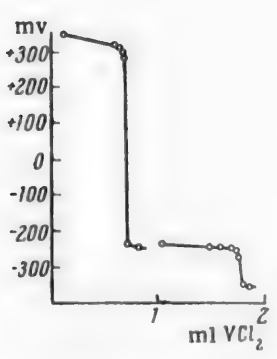
Thallium, mg		Error, mg	Thallium, mg		Error, mg
taken	found		taken	found	
5,14	5,13	−0,01	2,57	2,60	+0,03
5,14	5,19	+0,05	2,57	2,57	0
4,12	4,10	−0,02	1,03	1,06	+0,03
4,12	4,11	−0,01	1,03	1,03	0

TABLE 2. Determination of Thallium in the Presence of Foreign Cations

Taken, mg				Ratio Tl:Me	Tl found, mg	Error, mg
Tl	Cd	Zn	Pb			
5,14	500	—	—	1 : 100	5,09	−0,05
2,57	250	—	—	1 : 100	2,54	−0,03
3,86	1150	—	—	1 : 300	3,82	−0,04
2,57	1500	—	—	1 : 600	2,60	+0,03
2,57	3000	—	—	1 : 1200	2,64	+0,07
3,86	—	2300	—	1 : 600	3,86	0
5,14	—	—	2600	1 : 500	5,13	−0,01
2,06	600	600	600	1 : 300 : 300 : 300 (1 : 900)	2,11	+0,05
2,06	400	400	400	1 : 200 : 200 : 200 (1 : 600)	2,05	−0,01

TABLE 3. Determination of Thallium in Technical Materials

Sample	Wt. of sample, g	Tl found, %	Tl added, %	Amt. of Tl that should be present %	Tl found, %	Error, %
Bricketted cadmium (containing 0.15% Tl according to plant analysis)	1,3062	0,13	0,32	0,45	0,43	−0,02
	1,4028	0,17	0,15	0,32	0,32	0
	1,2216	0,17	0,42	0,59	0,58	−0,01
Slag	0,2142	1,16	0,96	2,12	2,15	+0,03
	0,2344	1,28	1,62	2,90	2,89	−0,01
	0,2308	1,21	1,50	2,71	2,68	−0,03



Titration of a mixture of 3.01 g of thallium and 3.14 mg of bismuth. 2.98 mg thallium and 3.14 mg bismuth found.

Determination of thallium in the presence of bismuth. We have already pointed out [1] that bismuth can be quantitatively determined by means of divalent vanadium. Despite the fact that bismuth is quantitatively separated by divalent vanadium from concentrated hydrochloric acid, nevertheless a sharp potential jump is observed during potentiometric titration in a medium of 1-3 N acid.

Bearing in mind the oxidation potentials of thallium and bismuth, one might expect that at an appropriate acidity, thallium should be reduced first and then bismuth. The technique for determining thallium and bismuth successively reduces to the following. To a solution of a trivalent thallium salt was added a known volume of a bismuth salt solution (or Bi_2O_3), and the acidity of the solution adjusted to the requisite value (6-10 N) for determination of thallium by means of sulfuric or hydrochloric acid. Titration was carried out with 0.05 N VCl_2 until the first potential jump was obtained. The solution was then diluted approximately three times with water and titration continued to the second potential jump corresponding to completion of reduction of bismuth. Since, during the titration of small amounts of thallium with 0.05 N VCl_2 solution, a microburet must be used in order to attain the highest accuracy, while the bismuth content may be many times greater than that of thallium, after the

first potential jump (determination of thallium) it is best to continue titration with 0.1 N VCl_2 solution measured out from a macroburet (determination of bismuth). The presence of large amounts of Cd, Zn, and Pb do not interfere with determination of thallium in bismuth. Results of these determinations are given in Table 4. The titration curves are shown in the diagram.

TABLE 4. Determination of Thallium and Bismuth in Each Others Presence

No.	Taken, mg		Found, mg		Error, mg	
	Tl	Bi	Tl	Bi	Tl	Bi
1	3,01	3,14	2,98	3,14	−0,03	0
2	2,57	3,49	2,62	3,54	+0,05	+0,05
3	1,51	301,5	1,53	299,7	+0,02	−1,8
4*	1,51	150,8	1,57	151,1	+0,06	−0,3

*160 mg Pb, 160 mg Cd, and 160 mg Zn were added to the amounts of Tl and Bi indicated.

We should like to thank V. G. Tiptsova a co-worker in Moscow University for her gift of bricketted cadmium and slag.

SUMMARY

It has been established that trivalent thallium can be determined potentiometrically by titration with a solution of a divalent vanadium salt in 6-10 N hydrochloric (sulfuric) acid.

A method has been developed for the successive determination of thallium and bismuth in each others presence.

Large amounts of Zn, Cd, and Pb do not interfere with thallium determination. The method can be used for analysis of industrial materials.

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THE POLAROGRAPHIC BEHAVIOR OF INDIUM IN THE PRESENCE OF TRIHYDROXYGLUTARIC ACID

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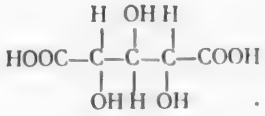
Translated from Zhurnal Analitcheskoi Khimii, Vol. 16, No. 5, pp. 555-561,
September-October, 1961
Original article submitted March 24, 1960

Compound of metals with trihydroxyglutaric acid have been studied to a limited extent. Falikov, Grigor'eva, and Davidenko [1-7] have studied the compounds of trihydroglutaric acid with iron, copper, nickel, cobalt, gallium, nd lanthanum, and have shown that the cations of trivalent elements can form electroneutral, cationic, and anionic complexes with trihydroxyglutaric acid. Davidenko [8] has studied the complex forming behavior of indium with trihydroxyglutaric acid by potentiometric titration, by measuring the electrical conductivity, and polarographically. The results of the polarographic study are only dealt with briefly in his article. The aim of our work was an all-round study of the polarographic behavior of indium over a wide pH range in the presence of a series of organic dicarboxylic acids and hydroxy acids [9], including trihydroxyglutaric acid.

EXPERIMENTAL

Indium perchlorate was prepared by dissolving indium metal in concentrated perchloric acid.

Trihydroxyglutaric acid. We used the optically inactive isomer, xylotrihydroxyglutaric acid



The trihydroxyglutaric acid was recrystallized twice from water. The melting point of the acid was 137-139°. 0.5 M solutions of the acid were prepared by dissolving aliquots.

Measurements were made on a Heyrovsky automatic polarograph (galvanometer sensitivity $3.83 \cdot 10^{-9}$ amp/mm/m) at a temperature of 25 ± 0.2°. A saturated calomel electrode was used as anode. Since the waves obtained for indium in the presence of trihydroxyglutaric acid do not have maxima, there is no need to add any surface active materials.

When the acidity of the medium is changed from pH 1 to pH 4 (by addition of NaOH or $HClO_4$), indium gives well defined waves in the presence of 0.1 M trihydroxyglutaric acid. The height of the diffusion wave drops with increasing pH (Table 1); the indium wave is hardly noticeable at pH 5, while at pH 7.37 upwards it disappears completely. Nevertheless, in an alkaline medium, in the presence of excess sodium trihydroxyglutarate, indium hydroxide is not precipitated and the solution remains clear. At pH 11 a wave appears again, but at a more negative potential. The half-wave potential is shifted toward the negative side with increasing pH (Table 1, Fig. 1).

The decrease in the indium wave height with increasing pH, and also the fact that the wave even disappears between pH 7 and 11, led us to assume that indium in the form of some basic salt or hydroxide changes into a colloidal state. Using an ultramicroscope, we examined several solutions of indium in trihydroxyglutaric acid at various pH values, and found that in a $4 \cdot 10^{-4}$ M solution of indium in 0.1 M trihydroxyglutaric acid large amounts of colloidal particles could be observed. It was found that the concentration of colloidal particles is appreciably greater in solutions with pH 6, 7, 9, and 10 than in solutions with pH 2 and 3; this confirmed our assumption re the formation of a colloidal solution.

We studied the relation between $E_{\frac{1}{2}}$ of indium and the trihydroxyglutaric acid at pH 2, 3, and 4. Since the dissociation of trihydroxyglutaric acid changes with changes in the acidity of the medium, we calculated the percentage composition of the undissociated molecules of trihydroxyglutaric acid $[RH_2]$, as well as of uni- $[RH]^-$ and

disubstituted $[R]^{2-}$ ions as a function of pH (Table 2). For these calculations we used the values of the dissociation constants of trihydroxyglutaric acid found by Grigor'eva [10], $K_1 = 5.1 \cdot 10^{-4}$ and $K_2 = 3 \cdot 10^{-5}$.

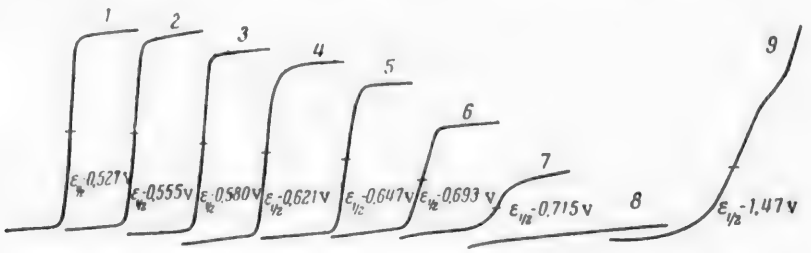


Fig. 1. The change in $E_{\frac{1}{2}}$ and in the value of the diffusion current of indium with pH, in the presence of trihydroxyglutaric acid (0.1 M) $[In^{III}] = 4 \cdot 10^{-4}$ M. 1) pH 1.62; 2) 2.33; 3) 2.99; 4) 4.02; 5) 4.41; 6) 4.88; 7) 5.45; 8) 7.36; 9) pH 11.

TABLE 1. The Relation between $E_{\frac{1}{2}}$ and the Values of the Diffusion Current and pH (in the presence of Na^+ or NH_4^+)

pH	$E^1/_2$, b	i, мм	pH	$E_{1/2}$, b	i, мм	pH	$E_{1/2}$, b	i, мм	pH	$E_{1/2}$, b	i, мм
1,62	—0,527	53	4,02	—0,621	46	5,45	—0,715	12	~ 9	—	—
2,33	—0,555	52	4,41	—0,647	40	7,36	—	—	~10	—	—
2,99	—0,580	49	4,88	—0,693	28	~8	—	—	11	—1,47	40

TABLE 2. The Relation between $E_{\frac{1}{2}}$ and Trihydroxyglutaric Acid Concentration at pH 2, 3, and 4. $[In^{3+}] = 4 \cdot 10^{-4}$ M

pH	C_{THG}, M	C_{RH^-}, M	$C_{R_2^-}$, M	$C_{RH^-} + R^{2-}$	$E_{\frac{1}{2}}$, v
2,00	0,05	$2,5 \cdot 10^{-3}$	$7,3 \cdot 10^{-6}$		—0,548
2,10	0,07	$3,4 \cdot 10^{-3}$	$1,0 \cdot 10^{-5}$		—0,548
2,00	0,10	$4,9 \cdot 10^{-3}$	$1,5 \cdot 10^{-5}$		—0,548
2,00	0,15	$7,3 \cdot 10^{-3}$	$2,2 \cdot 10^{-5}$		—0,548
1,99	0,20	$9,7 \cdot 10^{-3}$	$2,9 \cdot 10^{-5}$		—0,548
2,01	0,30	$1,5 \cdot 10^{-2}$	$4,4 \cdot 10^{-5}$		—0,552
2,03	0,40	$1,9 \cdot 10^{-2}$	$5,8 \cdot 10^{-5}$		—0,567
3,01	0,05	$1,7 \cdot 10^{-2}$	$5,0 \cdot 10^{-4}$		—0,583
3,00	0,07	$2,3 \cdot 10^{-2}$	$7,0 \cdot 10^{-4}$		—0,583
3,02	0,10	$4,0 \cdot 10^{-2}$	$1,0 \cdot 10^{-3}$		—0,583
3,00	0,15	$5,0 \cdot 10^{-2}$	$1,5 \cdot 10^{-3}$		—0,583
2,98	0,20	$7,0 \cdot 10^{-2}$	$2,0 \cdot 10^{-3}$		—0,583
3,01	0,30	$1,0 \cdot 10^{-1}$	$2,9 \cdot 10^{-3}$		—0,590
3,00	0,40	$1,3 \cdot 10^{-1}$	$3,9 \cdot 10^{-3}$		—0,590
3,99	0,07	$4,7 \cdot 10^{-2}$	$1,4 \cdot 10^{-2}$	$6,0 \cdot 10^{-2}$	—0,609
4,01	0,10	$6,7 \cdot 10^{-2}$	$2,0 \cdot 10^{-2}$	$9,0 \cdot 10^{-2}$	—0,615
4,00	0,15	$1,0 \cdot 10^{-1}$	$3,0 \cdot 10^{-2}$	$1,3 \cdot 10^{-1}$	—0,622
4,00	0,20	$1,3 \cdot 10^{-1}$	$4,0 \cdot 10^{-2}$	$1,7 \cdot 10^{-1}$	—0,627
4,02	0,30	$2,1 \cdot 10^{-1}$	$6,1 \cdot 10^{-2}$	$2,6 \cdot 10^{-1}$	—0,635
4,01	0,40	$2,7 \cdot 10^{-1}$	$8,1 \cdot 10^{-2}$	$3,5 \cdot 10^{-1}$	—0,642

The relation between the half-wave potential and the trihydroxyglutaric acid concentration at pH 2 and ionic strength $\mu = 0.32$, at pH 3 and ionic strength $\mu = 0.12$, and also at pH 4 and $\mu = 0.32$ is given in Table 2.

At pH 2, 3, and 4 the waves have the form of waves corresponding to a reversible reduction process on the electrode. The reversibility of the process was checked on the basis of the constancy of the slope of the straight lines to the axes within the coordinates $\log (i/i_\alpha - i) - E$ and was also checked on an apparatus constructed by Sochevanov and Lyubimova [11] using Kalousek's method [12, 13] (Fig. 2). At pH 3 and 4, at a constant trihydroxyglutaric acid

concentration and constant ionic strength, the value of the diffusion current is proportional to the indium concentration in solution; accordingly, indium can be determined polarographically in a supporting electrolyte of trihydroxyglutaric acid.

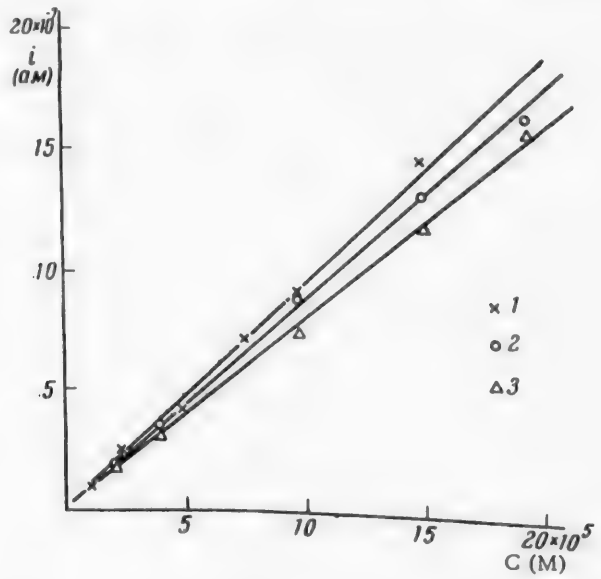


Fig. 2. Verification of the reversibility of the reduction process of indium in the presence of trihydroxyglutaric acid at pH 4 and pH 11. 1) Cathode wave at pH 4; 2) reversible anode-cathode wave of indium at pH 4; 3) cathode wave of indium at pH 11; 4) anode-cathode wave of indium at pH 11.

TABLE 3. Half-Wave Potentials of Some Elements in 0.1 M Trihydroxyglutaric Acid at pH 3*

Elements	$E_{\frac{1}{2}}$, v (relative to the saturated calomel electrode)
Tl^{I}	—0,397
Pb^{II}	—0,473
Cd^{II}	—0,662
In^{III}	—0,610
As^{III}	—0,775
Al^{IV}	Not reduced
Ga^{III}	Not reduced

*Tin (II) and antimony (III) hydrolyze at pH 3.

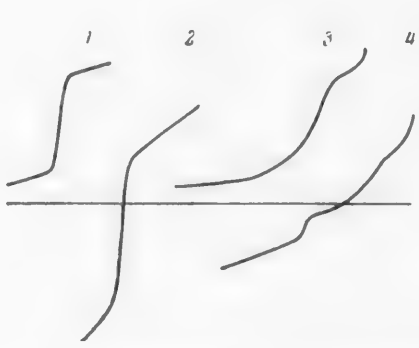


Fig. 3. Calibration curves for determination of cadmium and indium. 1) For indium at pH 3; 2) for cadmium at pH 3; 3) for cadmium at pH 9.

Although the half-wave potentials of cadmium and indium are very close in trihydroxyglutaric acid (Table 3), we have been able to develop a method for determining indium and cadmium in each others presence. According to our results, indium at pH 8 and 9 in the presence of ammonium trihydroxyglutarate does not give a wave, while cadmium under the same conditions gives a wave at a potential of −0.63 v. The solution containing a mixture of indium and cadmium salts in the presence of trihydroxyglutaric acid is adjusted to pH 3 and the total polarographic wave of indium and cadmium is taken. NH_4OH is then added to the solution until the pH is 9 (adjusted to a weak

rose color of phenolphthalein) and just the cadmium wave taken. The three following calibration curves are then constructed: 1) a calibration curve for an indium solution at pH 3; 2) a calibration curve for cadmium at pH 3; 3) a calibration curve for cadmium at the same concentrations but at pH 9 (Fig. 3). From the wave height of the test cadmium solution at pH 9 and using calibration curve 3, the corresponding cadmium concentration is found. Then, knowing the cadmium concentration, the wave height for the given cadmium concentration at pH 3 is found by means of calibration curve 2. Next, the cadmium wave height thus found is subtracted from the total wave for indium and cadmium, and the wave height for indium determined. Finally, using calibration curve 1, and knowing the height of the indium wave, the indium concentration is found.

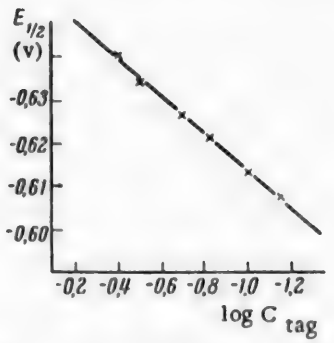


Fig. 4. The relation between $E_{\frac{1}{2}}$ for indium and the logarithm of trihydroxyglutaric acid concentration at pH 4. $[In^{III}] = 4 \cdot 10^{-4}$ M; $\mu = 0.32$.

Results of such determinations are given in Table 4.

In an alkaline medium in the presence of trihydroxyglutarate at pH 11, an indium wave appears with $E_{\frac{1}{2}} = -1.47$ v. Under the same conditions, but in the absence of trihydroxyglutarate, indium hydroxide immediately precipitates out and this precipitate only dissolves in 5 N NaOH. The half-wave potential in this solution is -1.17 v; this led us to assume that the indium wave which appears in trihydroxyglutarate and which has $E_{\frac{1}{2}} = -1.47$ v, is the wave of a very stable complex of indium with trihydroxyglutarate.

A change in the concentration of the trihydroxyglutarate anion in a strongly alkaline medium leads to a displacement of the half-wave potential (Table 5).

We examined the effect of a further increase in NaOH concentration on the nature of the reduction of indium, and found that on changing the NaOH concentration from 0.5 M to 5.0 M the half-wave potential does not alter. The wave height decreases to some extent with increasing alkali concentration; this is caused by an increase in the viscosity of the solution.

TABLE 4. Polarographic Determination of Indium and Cadmium in Each Others Presence

Taken, mg		Ratio by wt.	Found, mg		Error, %	
In	Cd		In	Cd	In	Cd
0,065	0,065	1 : 1	0,061	0,064	—6,1	—1,5
0,108	0,109	1 : 1	0,103	0,111	—4,5	+1,8
0,076	0,153	1 : 2	0,074	0,142	—2,6	—7,2
0,043	0,174	1 : 4	0,041	0,170	—4,7	—2,3
0,162	0,109	1,5 : 1	0,165	0,102	+1,9	—6,4
0,135	0,031	4,5 : 1	0,125	0,031	+7,4	±0,0
0,270	0,031	9 : 1	0,251	0,031	—7,0	±0,0
2,700	0,031	90 : 1	2,540	0,031	—5,9	±0,0

TABLE 5. The Relation between $E_{\frac{1}{2}}$ and Trihydroxyglutaric Acid Concentration in 1 N NaOH and at $\mu = 1.8$

C_{THG}, M	$C_{R^{2-}}$, M	$E_{\frac{1}{2}}$	C_{THG}, M	$C_{R^{2-}}$, M	$E_{\frac{1}{2}}$
0,40	0,40	—1,50	0,10	0,10	—1,47
0,20	0,20	—1,49	0,05	0,05	—1,46

In 1 N NaOH, for a trihydroxyglutaric acid concentration of 0.1 M and at an ionic strength of $\mu = 1.1$, the linear relation between the value of the diffusion current and indium concentration is preserved; indium can therefore be determined in such a supporting electrolyte.

Nevertheless, the half-wave potentials of some ions in a supporting electrolyte of 0.1 M trihydroxyglutaric acid and 1 N NaOH (Table 6) show that determination of indium in the presence of trihydroxyglutaric acid in a strongly alkaline medium does not have any advantages.

DISCUSSION

A regular displacement of the half-wave potential $E_{\frac{1}{2}}$ of indium with changes in trihydroxyglutaric acid concentration is only observed at pH 4 (Table 2). A small displacement of the half-wave potential at pH 2 and 3 is only observed at trihydroxyglutaric acid concentrations in excess of 0.2 M, 500 and more times greater than the indium concentration. It can be assumed that at pH 2 and 3 a very strongly dissociating complex of indium with trihydroxyglutaric acid is formed.

TABLE 6. Half-Wave Potentials of Some Ions in a 0.1 M Trihydroxyglutaric Acid Solution in 1 N NaOH

Ions	$E_{\frac{1}{2}}$ (first wave), v relative to the saturated calomel electrode	$E_{\frac{1}{2}}$ (second wave), v	Ions	$E_{\frac{1}{2}}$ (first wave), v relative to the saturated calomel electrode	$E_{\frac{1}{2}}$ (second wave), v
In^{III}	—1,47		Sn^{II}	—0,77	
Zn^{II}	—1,47		As^{III}	—1,36	
Pb^{III}	—0,77		Al^{III}	—1,42	
Tl^{I}	—0,47		Ga^{III}	Not reduced	
Sb^{III}	—1 31		Gd^{II}	—0,80	—1,30

At pH 4, $E_{\frac{1}{2}}$ is shifted toward negative potentials with increasing trihydroxyglutaric acid concentration.

At pH 4 the concentration of RH^- ions only increases insignificantly, but the concentration of R^{2-} ions increases by more than one order. On the basis of these facts one can conclude that the stable complexes which lead to an appreciable shift in $E_{\frac{1}{2}}$ are formed from indium and the R^{2-} ions of trihydroxyglutaric acid and not from indium with the RH^- ions and even less so with undissociated molecules of the acid. This conclusion agrees with Davidenko's results [8]. The relationship between the changes in $E_{\frac{1}{2}}$ with changes in trihydroxyglutaric acid concentration at pH 4 is illustrated by the straight line in Fig. 4. The coordination number P which we calculated at pH 4 was 2.1.

$$P = \frac{\Delta E_{1/2} \cdot n}{\Delta \lg C_x \cdot 0{,}059} = \frac{0{,}0265 \times 3}{0{,}62 \times 0{,}059} = 2{,}1.$$

Davidenko [8] gives results for the relationship between $E_{\frac{1}{2}}$ and trihydroxyglutaric acid at pH 1.5. He concludes that "the shift in potential corresponds to formation of a 1:1 compound." We do not think that this is quite correct. According to his results, the relationship between $E_{\frac{1}{2}}$ and the logarithm of trihydroxyglutaric acid concentration is not expressed by a straight line, but by an arc-shaped curve. By meaning the results one can produce a straight line with any slope. It would seem to us that the linear relationship is most clearly expressed for trihydroxyglutaric acid concentrations of 0.4, 0.6, and 0.8 M. On the basis of these results the value calculated for the coordination number is approximately 2.3 and not 1:

$$P = \frac{0{,}014 \cdot 3}{0{,}3 \cdot 0{,}059} = 2{,}3$$

and, consequently, the potential shift corresponds to a compound with a molar ratio of 1:2, in agreement with our results for the compound formed at pH 4.

In order to calculate the instability constant of the complex indium ion it is necessary to know the half-wave potential of the simple indium ion, e.g., in a $HClO_4$ medium. Since reduction of In^{3+} in $HClO_4$ is an irreversible process, we adopted the method of amalgam polarography.

Using an electrode in the form of a stationary drop of indium amalgam, we determined the half-peak potential during anodic dissolution of indium from the amalgam in a supporting electrolyte of 0.1 M $HClO_4$, and found it to be equal to −0.488 v. The value which we found agrees with the value of $E_{\frac{1}{2}}$ found by Cozzi and Raspi [14] by extrapolation (−0.485 ± 0.002 v).

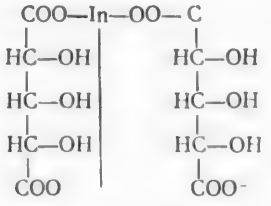
Table 7 contains results of the calculation of the instability constant, taking into account only the concentration of the doubly charged anions $C = C_{R^-}$. On taking into account the sum of uni- and dicharged ions $C_x - C_{R^-} + RH^-$ the mean value of $K = (1.87 \pm 0.11) \cdot 10^{-9}$.

TABLE 7. Values of the Instability Constant of the Complex of Indium with Trihydroxyglutaric Acid

Concentration C_x, M	$E_{\frac{1}{2}}$, v	log K	pK	K
0,061	—0,635	—10,05	10,05	$8,91 \times 10^{-11}$
0,040	—0,627	—10,00	10,00	$1,00 \times 10^{-10}$
0,030	—0,622	—10,00	10,00	$1,00 \times 10^{-10}$
0,020	—0,615	—10,00	10,00	$1,00 \times 10^{-10}$

K (mean) = $(9,73 \pm 0,82) \times 10^{-11}$.

The charge of the complex of indium with 0.1 N trihydroxyglutaric acid at pH 4, as an electrophoresis method showed [1], was negative. Our experiments did not confirm Davidenko's assertion that neutral indium complexes should be present in a weakly acid medium. Bearing in mind the value p = 2, and the negative charge of the complex compound, one can assume that under our conditions In^{III} gives a complex compound of the following structure with trihydroxyglutaric acid:



In an alkaline medium (pH 11) in the presence of trihydroxyglutarate, indium forms a stable complex compound with $E_{\frac{1}{2}} = -1.47$ v. It is possible that indium is connected to the hydroxyl ions in this compound. The polarogram obtained by Kalousek's method (Fig. 3) shows that reduction of indium in the presence of trihydroxyglutaric acid in an alkaline medium is an irreversible process. We were unable to therefore to determine the coordination number polarographically and to determine the instability constant of this complex compound.

SUMMARY

The polarographic behavior of indium in the presence of trihydroxyglutaric acid has been examined in acid, neutral, and alkaline media.

The value of the half-wave potential of the simple indium ion in $HClO_4$ has been determined by measuring the value of the half-peak potential during anodic dissolution of indium from an amalgam. The half-wave potential was found to be −0.488 v.

The effect of trihydroxyglutaric acid concentration on $E_{\frac{1}{2}}$ for indium has been examined; it has been found that regular displacement of $E_{\frac{1}{2}}$ with changes in trihydroxyglutaric acid concentration is only observed at pH 4 and pH 11. It has been established that the coordination number p = 2, while it has been found that the instability constant of the complex compound formed between indium and trihydroxyglutaric acid at pH 4 has a value K (mean) = $= (9.73 \pm 0.82) \cdot 10^{-11}$.

It has been established that reduction of indium at pH 11 is an irreversible process.

A method is suggested for the polarographic determination of indium and cadmium in each others presence by using trihydroxyglutaric acid as supporting electrolyte at pH 3 and pH 9.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 18. THE THIOOXINATES OF GALLIUM, INDIUM, AND THALLIUM

PHOTOMETRIC DETERMINATION OF INDIUM WITH THIOOXINE*

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 562-572, September-October, 1961
Original article submitted August 15, 1960

The analytical chemistry of gallium, indium, and thallium has still not been developed sufficiently well. This is particularly true of methods of separating and determining gallium and indium [1]. Accordingly, the synthesis of new complex compounds, and the search for more selective reagents for these elements is of great practical importance.

As a result of studies of the analytical properties of 8-mercaptoquinoline (thiooxine) we have found that under certain conditions this reagent permits determination of microgram amounts of indium in the presence of overwhelming amounts of certain elements which usually interfere with the determination of this element by other methods.

Preparation and composition of gallium, indium, and thallium thiooxinates. Gallium salts in very weakly acid, neutral, and alkaline solutions form with thiooxine an amorphous looking orange-yellow precipitate. It can be obtained in a crystalline state from hot aqueous-alcoholic solutions. A hot solution of 0.12 g of gallium trichloride in 25 ml of 65% ethanol is added dropwise and with stirring to a filtered solution of 1.1 g sodium thiooxinate in 55 ml of 90% ethanol which has been heated to the boil. When the solutions are poured together the mixture acquires a dark-red color and an orange-yellow, crystalline precipitate of gallium thiooxinate rapidly settles out. The precipitate is filtered off through a glass filter crucible, washed several times with ethanol, and dried in air. After recrystallization from dimethylformamide the precipitate has the following composition:

Found %: Ga 12.44; N 7.50; S 17.63. $Ga(C_6H_6NS)_3$. Calculated %: Ga 12.67; N 7.64; S 17.47.

Indium salts in weakly acid, neutral, and alkaline solutions interact with thiooxine to form a yellow, amorphous looking precipitate. The precipitate can be obtained in a crystalline form from hot aqueous-alcoholic solutions. A hot solution of 0.12 g of indium trichloride in 30 ml of 40% ethanol is added dropwise and with stirring to a filtered solution of 1 g of sodium thiooxinate in 40 ml of 80% ethanol which has been heated to the boil. The yellow, crystalline precipitate which gradually settles out is filtered off through a glass crucible, washed several times with hot alcohol, and dried in air. On recrystallization from dimethylformamide the preparation has the following composition:

Found %: N 7.17; S 16.26; H 3.26. $In(C_9H_6NS)_3$. Calculated %: N 7.05; S 16.50; S 3.04.

It does not contain water of crystallization.

It has been shown earlier [2, 3] that trivalent thallium is reduced by thiooxine to its univalent state with formation of thallium (I) thiooxinate. Thallous thiooxinate can be prepared in the crystalline state from aqueous-pyridine solutions. A hot solution of 1.3 g of CH_3COOTl in 5 ml of pyridine is added dropwise to a solution of 4 g of sodium thiooxinate in a mixture of 5 ml of water and 25 ml of pyridine heated to the boil. The orange crystalline precipitate which settles out is removed by suction on a filter, washed several times with methanol, and dried in air.

Thallous thiooxinate can also be prepared in a crystalline state from ethanol-water media as in the case of gallium thiooxinate.

* For communication 17, see Zh. analit. khimii 16, 150 (1961).

Found %: N 3.80; S 8.75; H 1.69. C_9H_6NS-Tl. Calculated %: N 3.84; S 8.78; H 1.64.

Determination of active hydrogen in the preparation dried at 150° showed the absence of water of crystallization.

During measurements of the molar extinction coefficients of solutions of the thiooxinates of various elements, a feature which attracted attention was the too low molar extinction coefficient of gallium thiooxinate compared with the molar extinction coefficients of the other thiooxinates of trivalent elements and elements containing three molecules of thiooxine in the molecule. These depressed values of the molar extinction coefficients are observed both in solutions of the crystalline samples of gallium thiooxinate, and in solutions obtained by extraction from the aqueous phase. It was natural to assume that the gallium thiooxinate formed in solution is not identical to the crystalline thiooxinate. In this connection therefore we determined the composition of thiooxinates in solution. The low molar extinction coefficient of crystalline gallium thiooxinate, however, remained incomprehensible, since there was no doubt about the accuracy of the analyses of the crystalline samples. Repeated analyses of various preparations always gave results corresponding to the formula $Ga(C_9H_6NS)_3$. The reason for this low value of the molar extinction coefficient of solutions of gallium thiooxinate became apparent on studying the absorption spectra.

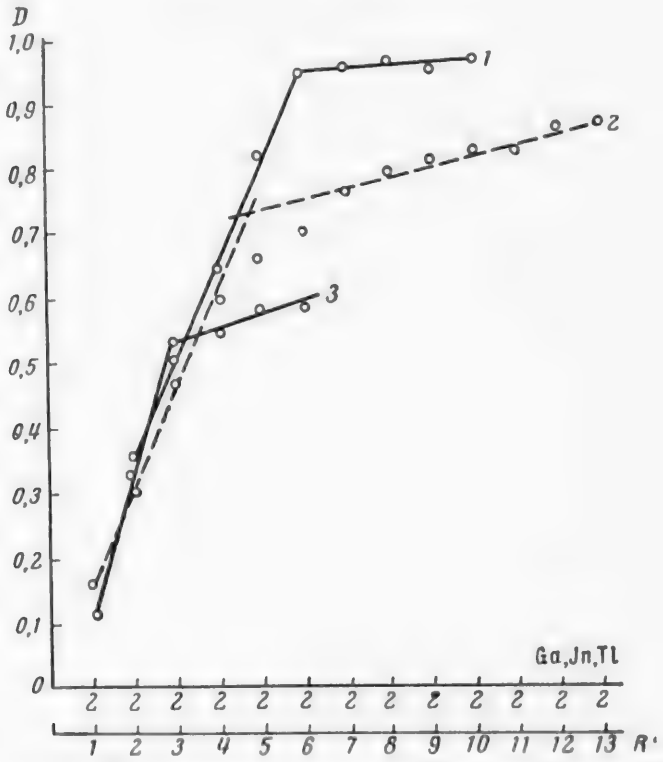


Fig. 1. Composition of gallium, indium, and thallium thiooxinates in a toluene extract. 1) Indium thiooxinate; 2) gallium thiooxinate; 3) thallium thiooxinate.

The composition of the thiooxinates in solution was determined by the isomolar series method. Forty ml of a borate buffer solution with pH 8 was introduced into a separating funnel; varying amounts of a 0.001 M solution of sodium thiooxinate (ml) which were gradually increased from experiment to experiment and a constant amount (ml) of a 0.001 g ion/liter solution of gallium were then added. The gallium thiooxinate formed was extracted with 20 ml of chloroform for 3 min. The chloroform extract was transferred to a 1 cm cell, and its optical density measured on a SFD-1 spectrophotometer at 397 mμ (λ_{max} of gallium thiooxinate, Figs. 2 and 3). The reference solution was a chloroform extract obtained on using the same amounts of reagents but omitting gallium. As is evident from Fig. 1, there is a break which is not sharp at Ga : R = 1 : 2, which testifies to the formation of a complex of the composition

$Ga(C_9H_6NS)_2Cl$ with low stability, or, bearing in mind its reasonably good solubility in a series of organic solvents, to the formation of a basic thiooxinate $Ga(C_9H_6NS)_2OH$, since the reaction was carried out in an alkaline medium.

The composition of indium thiooxinate was determined by the same method. To various amounts (ml of 0.001 M sodium thiooxinate at pH 7 which were increased from experiment to experiment was added a constant amount (ml) of an indium solution with a concentration of 0.001 g·ion/liter. The indium thiooxinate formed was extracted with 20 ml of chloroform, and its optical density on a SFD-1 spectrophotometer at 407 mμ (λ_{max} of indium thiooxinate, Figs. 2 and 3). The reference solution was a chloroform extract obtained on using the same amounts of reagents but omitting indium. Figure 1 shows that the sharp break on the curve corresponds to a composition of $In(C_9H_6NS)_3$ for indium thiooxinate.

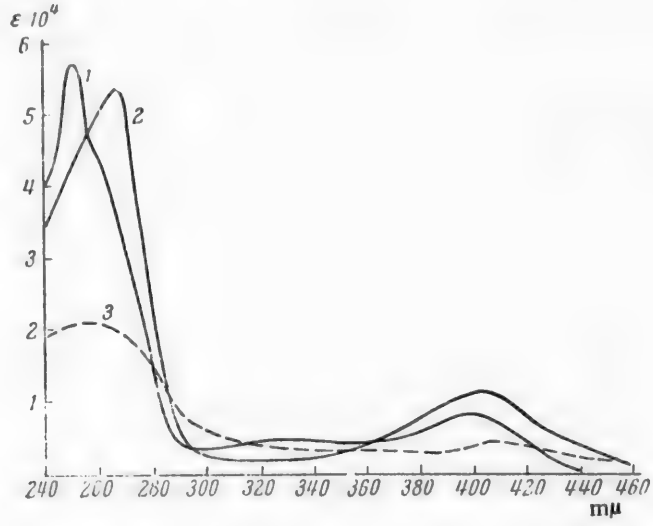
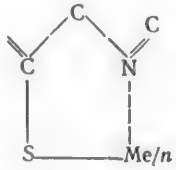


Fig. 2. Absorption spectra of gallium, indium, and thallium thiooxinates in chloroform. 1) $Ga(C_9H_6NS)_3$ λ_{max} 252 mμ, 324 and 397 mμ; 2) $In(C_9H_6NS)_3$ λ_{max} 268 and 407 mμ; 3) C_9H_6NSTl λ_{max} 250 and 406 mμ.

The composition of thallium thiooxinate was determined at pH 9.5 using a 0.001 M solution of thiooxine and a solution of a thallous salt with a concentration of 0.001 g ion/liter. The optical density of the chloroform extract was measured at 406 mμ (λ_{max} thallium thiooxinate, Figs. 2 and 3). The break on the curve which is not sharp (Fig. 1) testifies (as in the case of gallium thiooxinate) to the very low stability of the complex found between Tl : R = = 1 : 1 and Tl : r = 1 : 1/3. These results indicate a composition of C_9H_6NSTl for the complex.

Absorption spectra and molar extinction coefficients of gallium, indium, and thallium. As the data in Table 1 show, most of the solvents which are suitable for work in the far ultraviolet do not dissolve gallium, indium, and thallium thiooxinates. Only chloroform is a suitable solvent and permits spectra to be taken at wavelengths higher than 245 mμ. In the other solvents the spectra can only be taken in the near ultraviolet.

An aliquot of the corresponding thiooxinate was dissolved in purified chloroform, and the optical density measured on a SF-4 spectrophotometer relative to chloroform. As Figs. 2 and 3 show (long wave maxima at higher concentrations of the thiooxinates are shown in Fig. 3), the absorption spectra of gallium and indium thiooxinates have three maxima each, while thallium has two. The maxima in the far ultraviolet (Ga, 252 mμ; In, 268 mμ, Tl, 250 mμ) belong to the quinoline nucleus, while the maxima on the boundary of the ultraviolet and visible regions (Ga, 397 mμ; In, 407 mμ; Tl, 406 mμ) belong to the cyclic group



where Me = Ga, In, Tl; n is the valence of the element. The maximum at 324-325 mμ for gallium thiooxinate, and the weak maximum for indium thiooxinate belong to the thiooxinate ion $C_9H_6NS^-$ formed as the result of the dissociation of the molecules of the thiooxinates:

$$Ga(C_9H_6NS)_3 \rightarrow Ga(C_9H_6NS)_2^+ + C_9H_6NS^-$$

$$In(C_9H_6NS)_3 \rightarrow In(C_9H_6NS)_2^+ + C_9H_6NS^-$$

This is quite clear from the absorption spectrum of sodium thiooxinate in ethanol (Fig. 3, curve 6), the absorption maximum of which at 324-325 mμ corresponds with the absorption maxima of gallium and indium thiooxinates in chloroform.

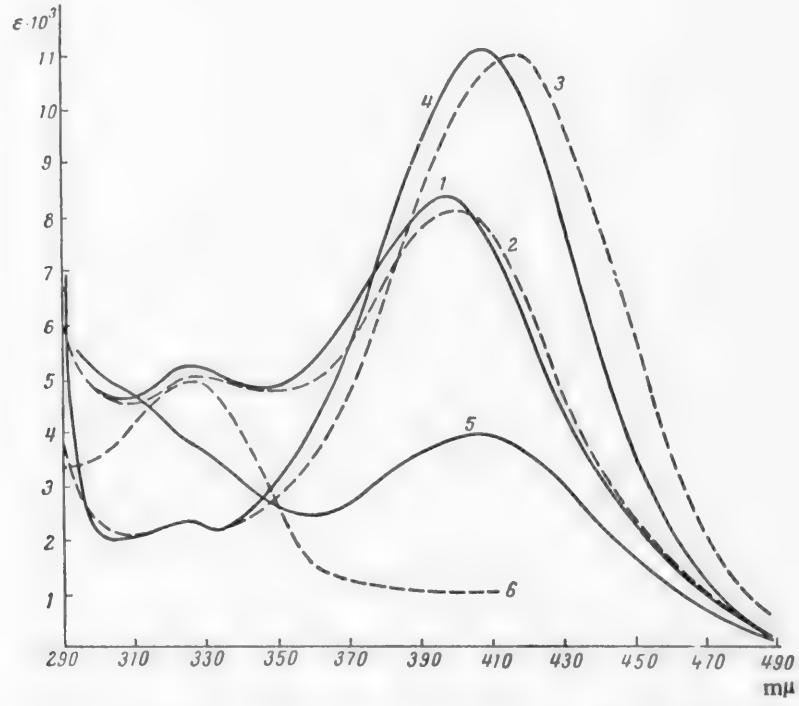


Fig. 3. Absorption spectra in the near ultraviolet of gallium, indium, and thallium thiooxinates. 1) $Ga(C_9H_6NS)_3$ in chloroform; λ_{max}, 324 and 397 mμ; 2) $Ga(C_9H_6NS)_3$ in toluene, λ_{max}, 324 and 400 mμ; 3) $In(C_9H_6NS)_3$ in toluene; λ_{max}, 324 and 418 mμ; 4) $In(C_9H_6NS)_3$ in chloroform; λ_{max}, 324 and 407 mμ; 5) C_9H_6NSTl in chloroform; λ_{max}, 406 mμ; 6) sodium thiooxinate in ethanol.

Solutions of the crystalline thiooxinates in purified chloroform were prepared in order to determine the molar extinction coefficients. The optical density of the solutions was measured relative to chloroform on a SF-4 spectrophotometer at the absorption maxima of the thiooxinates. The mean values of the molar extinction coefficients, obtained from many experiments at different concentrations of the thiooxinates in chloroform, were as follows: gallium thiooxinate $Ga(C_9H_6NS)_3$ — ϵ = 8400; indium thiooxinate $In(C_9H_6NS)_3$ — ϵ = 11,100; thallium thiooxinates C_9H_6NS-Tl approximately 4000. The type of solvent used has almost no effect on the value of the molar extinction coefficient.

The values of the extinction coefficients of the thiooxinates are approximately proportional to the amount of combined molecules of thiooxinate. In particular, the molar extinction coefficients of the thiooxinates into whose composition three molecules of thiooxine enter, are approximately 12,000. In such a case the molar extinction coefficients of $Ga(C_9H_6NS)_3$ and $In(C_9H_6NS)_3$, as long as their composition remains unchanged should also be equal to

about 12,000. From this point of view, the molar extinction coefficient of indium thiooxinate is slightly low, while the molar extinction coefficient of gallium thiooxinate corresponds to that of a thooxinate containing only two molecules of thiooxine. This is in good agreement with the interpretation advanced above of the absorption spectra and to the equations for the dissociation of thiooxinates.

TABLE 1. Solubility of the Crystalline Thiooxinates of Gallium, Indium, and Thallium in Organic Solvents

Solvent	Thiooxinate			Solvent	Thiooxinate		
	Ga	In	Tl		Ga	In	Tl
Chloroform	r.s.	r.s.	s.	Ethanol	i.	i.	i.
Bromoform	r.s.	r.s.	r.s.	Nonyl alcohol	i.	i.	i.
Bromobenzene	r.s.	r.s.	r.s.	Carbon tetrachloride	s.s.	s.s.	s.s.
Pyridine	r.s.	r.s.	r.s.	Diisoamyl ether	i.	i.	i.
Dimethylformamide	r.s.	r.s.	r.s.	Acetoamyl ester	i.	i.	i.
Toluene	s.	s.	s.	Isoamyl alcohol	i.	i.	i.
Benzene	s.	s.	s.	Hexane	i.	i.	i.
Acetone	s.	s.	s.	Isooctane	i.	i.	i.
Dioxane	s.s.	s.s.	s.s.				

Notes: r.s. – readily soluble; s – soluble; s.s. – sparingly soluble; i – insoluble.

As Moeller and Cohnen [4] have shown, the 8-hydroxyquinolates of gallium, indium, and thallium also possess this capacity of breaking down in organic solvents. In chloroform solutions of the 8-hydroxyquinolates of gallium, indium, and thallium also an absorption maximum of 8-hydroxyqinoline appears with time as in the case of 8-mercaptoquinolates. Nevertheless, the 8-mercaptoquinolates undergo a solvolytic breakdown of this kind appreciably more rapidly; thus gallium 8-mercaptoquinolate splits off one molecule of 8-mercaptoquinoline almost instantaneously, while during extraction from aqueous solutions, a complex containing only two molecules of 8-mercaptoquinoline passes into the organic solvent.

Breakdown of gallium thiooxinate in which the thiooxine molecule is split off, even in an organic solvent medium, is not unexpected, since gallium has very similar properties to aluminum which does not in general form a salt with thiooxine in aqueous media.

The relationship between the extractability of gallium, indium, and thallium thiooxinates and pH. The relationship between the extractability of the thiooxinates and pH was studied as follows. Into a 200 ml separating funnel containing 30-40 ml of a buffer solution with the requisite pH was introduced the requisite amount (theoretical number of moles with respect to the element Ga(In): R = 1:3 and Tl: R = 1:1, or an excess number of moles) of sodium thiooxinate in the form of an aqueous solution; the solution of the test element was then added. When the theoretical amount of thiooxine was used, indium and thiooxine solutions with a concentration of 0.001 g ion/liter were used. When excess thiooxine was used, its concentration was increased. In order to ensure identical experimental conditions the total volume after mixing the solutions was 50 ml in each case. The thiooxinate formed was extracted for 3 min with 10 ml toluene. The toluene extract was filtered free from drops of water by passing it through a plug of cotton wool, and its optical density measured in a 1 cm cell on a FEK-N-54 photocolorimeter fitted with a violet filter. As Fig. 4 shows, the thiooxine concentration affects the range over which the thiooxinates can be extracted. When the theoretical amount of thiooxine is used (Ga: R = 1:30, even when the maximum amount of complex is formed at pH about 7) the extractability does not reach 100%. When a ten-fold excess of reagent is used, gallium thiooxinate is extracted over the range pH 6.5-10, while for a 100-fold excess of reagent it is extracted over the range pH 5.5-10. Further increases in the thiooxine concentration do not essentially affect completeness of extraction of gallium, particularly in acid solutions.

Thiooxine concentration affects the extrability of indium in the same way: when the theoretical amount of reagent is used (In: r = 1:3) only about 83% indium is extracted over the range pH 4-10, while when a ten-fold excess of reagent is used 100% extractability is observed over the range pH 4-13. Further increases in thiooxine concentration slowly extend the region over which indium thiooxinate is stable.

Figure 4 shows that thallium thiooxinate is only stable in alkaline solutions. When the theoretical amount of reagent is used, thallium is 100% extracted over the range pH 10-14, while for a ten-fold and 100-fold excess of reagent the corresponding pH ranges are 9-14, and 7.5-14.

Of considerable interest is a comparison of the relative stability of the 8-hydroxyquinolates and thiooxinates of gallium, indium, and thallium. Since the dissociation constants of gallium, indium, and thallium have not hitherto been determined, in order to have an approximate comparison, use can be made of the extractability ranges of the oxinates and thiooxinates. The following results are given in the literature. Lacroix [5] is of the opinion that extraction of gallium 8-hydroxyquinolate starts to be quantitative from pH 2. Lacroix's experiments, however, were only approximate. Sandell [6] has stated that quantitative extraction of gallium 8-hydroxyquinolate occurs over the pH range 2.6-3.0. According to other results [7], extraction of galliun 8-hydroxyqinolate is quantitative over the pH range 3.0-6.2.

Moeller [8] has found that the range over which indium 8-hydroxyquinolate is extracted quantitatively is pH 3.2-4.5. Milner [9] is of the opinion that in order to ensure complete extraction of indium 8-hydroxyquinolate, it is necessary to work in the range pH 3.5-4.5. Lacroix [5] does not agree with the authors mentioned above and considers that quantitative extraction of indium as its 8-hydroxyquinolate occurs over the pH range 3-5.

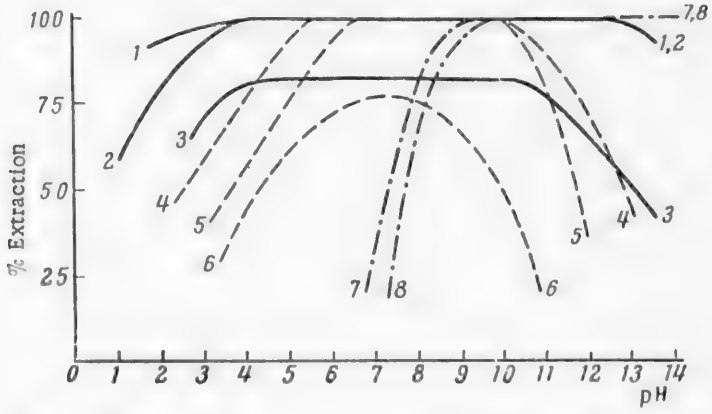


Fig. 4. The relationship between the extractability of gallium, indium, and thallium thiooxinates and pH. Indium: 1) 100-fold excess of thiooxine (R); 2) ten-fold excess of R; 3) theoretical amount of R; gallium: 4) 100-fold excess of R; 5) ten-fold excess of R; 6) theoretical amount of R; thallium: 7) ten-fold excess of R; 8) theoretical amount of R.

Apart from the disagreement between the results of different authors, another noteworthy feature is that the range of extraction of the 8-hydroxyquinolates of Ga and In is limited to weakly acid solutions and does not extend to the alkaline region as is the case for thiooxinates. The reason for this is that the authors mentioned above were interested in the extractability range for practical purposes, and, in this connection adjusted the requisite pH in the metal solution first and only then added 8-hydroxyqinoline. The consequence of this would be that the basic salts formed in weakly acid solutions, or the hydroxides formed in alkaline solutions,will not react with 8-hydroxyqinoline. The order in which the reagents are mixed has an essential effect on the extraction range (formation) of the complex salt.

To avoid this when working with thiooxine, as is evident from the technique described above, we added the solution of the test element dropwise to the buffered solution of thiooxine. Thus in the case of alkaline solutions we determined the relative rate of hydrolysis and formation of the thiooxinate. Moreover, in order to obtain comparable results, it is essential to determine the extractability range of the 8-hydroxyquinolates and thiooxinates under strictly analogous conditions – buffer solutions of the same composition and equal concentrations of reagents (8-hydroxyquinoline and thiooxine). In this connection we determined the extractability range of gallium and indium 8-hydroxyquinolates by the same method as that described above for thiooxinates, using a ten-fold excess of 8-hydroxyquinoline over that theoretically necessary for formation of the complex $Me(Ox)_3$. Gallium 8-hydroxyquinolate is extracted quantitatively over the range pH 5-13 (Fig. 5). It follows from these results that indium

thiooxinate (pH 4-13) is more stable than indium 8-hydroxyquinolate. Gallium 8-hydroxyquinolate, on the other hand is more stable than gallium thiooxinate (pH 6.5-10).

Bearing in mind the strong alkaline properties and the ready solubility in water of thallous hydroxide, one might expect that thallous 8-hydroxyquinolate will have low stability; this is confirmed by Moeller and Cohnen's work [10]. On the other hand, taking into account the poor solubility of Tl_2S, one might assume that its thiooxinate will have a relatively high stability. Actually, while Moeller and Cohnen [10] were only able to precipitate 0.87 g of thallium from 1 g of thallium in an alkaline medium with 8-hydroxyquinoline, using thiooxine, as can be seen from Fig. 4, it should be possible to extract microgram amounts of thallium quantitatively over the range pH 9-14.

Thus if one assumes that the stability of the bond Me(Ga, In, Tl)-N does not change in the 8-hydroxyquinolates and thiooxinates, one must conclude that the bond Ga–O is more stable than the bond Ga–S, while the reverse is true in the case of indium and thallium: the bonds In–S and Tl–S are more stable than the bonds In–O and Tl–O.

When a ten-fold excess of thiooxine is used over that theoretically necessary for formation of $In(C_9H_6NS)_3$, indium thiooxinate is extracted over the range pH 4-13. The wide range over which indium can be extracted permits one to determine this element both in weakly acid and in alkaline solutions. Determination of indium in weakly acid solutions does not have any practical importance, since most elements which form sulfides which are stable in aqueous media interact with thiooxine in weakly acid media. KSCN, KI, $CS(NH_2)_2$, KF, citrate, oxalate, thiosulfate, pyrophosphate, and sodium ethylenediaminetetracetate proved unsuitable for masking foreign elements in acid media.

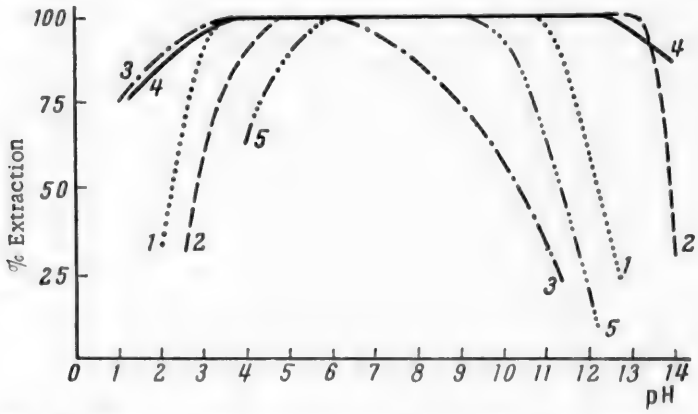


Fig. 5. The relationship between the extractability of gallium (1) and indium (2) 8-hydroxyquinolates and the pH of the medium (order in which the components were mixed: buffer + 8-hydroxyquinoline + metal). The relationship between the extractability of indium thiooxinate and the pH of the medium (3); order in which the components were mixed: indium + buffer + thiooxine. Effect of tartrate ions (14% solution of sodium tartrate) on the extractability range of indium (4) and gallium (5) thiooxinates.

Effect of cyanide and tartrate ions on completeness of extraction of indium and gallium thiooxinates. The pH range over which indium is extracted as its thiooxinate (pH 4-13) and which was found above, is only valid when an indium solution is added to a solution of thiooxine in a buffer medium with a definite pH. In actual practice one usually proceeds otherwise: the pH of the solution is established at the requisite value first and the reagent solution then added. When such a technique is adopted, in alkaline solutions hydroxides of basic salts of indium are formed which only partially interact with the thiooxine. Figure 5 shows the extractability curve of indium obtained by the method described above, but with the components mixed in the reverse order. As Fig. 5 shows, extraction of indium is quantitative only over the range pH 3.5-6. Formation of basic salts or hydroxides of indium can be prevented by addition of sodium tartrate, which is also necessary for keeping other metals in solution in an alkaline medium. The effect of the tartrate ion on the extractability range was examined as follows. Thirty-five ml of a 20% solution of neutral sodium tartrate and 10 ml (30 μg) of a solution of an indium (gallium) salt were introduced into a 200 ml

separating funnel. The pH was adjusted to the requisite value by means of NaOH or HCl solutions and the volume of the solution made up to 50 ml with water. One ml of a 1.25% solution of sodium thiooxinate at the same pH was then added. The thiooxinate formed was extracted by vigorous shaking with 10 ml of toluene. The extract was filtered through a plug of cotton wool and its optical density measured in a 1 cm cell on a FEK-N-54 photocolorimeter fitted with a violet filter. Pure toluene was used as the reference solution. The amount of indium (gallium) present was determined by means of a calibration curve constructed under conditions ensuring maximum extractability of the given thiooxinate, but without tartrate.

As Fig. 5 shows, in the presence of tartrate ions, indium is extracted over the range pH 4-12.5, while gallium is extracted over the range pH 6-10. These ranges coincide with the extractability ranges determined earlier under conditions which exclude hydrolysis of indium and gallium salts. This confirms the explanation given above for the very narrow extraction range for indium when no tartrate is used and when thiooxine is added after buffering the indium solution.

The effect of sodium tartrate concentration on the completeness of indium extraction was studied by the technique described above. The only difference in the experimental conditions was that the reaction was carried out in a buffer solution with pH 11, and that the amount of 20% sodium tartrate solution added was varied from experiment to experiment. It follows from these experiments that at pH 11, and for a total volume of 50 ml of solution, a minimum amount of 8 ml of 20% sodium tartrate solution is necessary for ensuring quantitative extraction of indium as its thiooxinate. Presumably, smaller amounts of tartrate cannot prevent formation of indium hydroxide or of basic indium salts. The rather high concentration of sodium tartrate required for preventing hydrolysis of the indium salts testifies to the low stability of the indium-tartrate complex.

The effect of varying concentrations of cyanide on the extractability of In and Ga was only studied in alkaline solutions. A definite volume of 40% KCN solution, 10 ml of indium (gallium) (30 μg) solution, and 1 ml of a 1.25% aqueous solution of sodium thiooxinate were introduced into a 200 ml separating funnel. The volume of the solution was made up to 50 ml and the thiooxinate formed extracted with 10 ml of toluene. The extract was filtered, and its optical density measured as described above. The experimental results show that even very high concentrations of cyanide ions in solution do not affect the extractability of indium, but the extent to which gallium is extracted falls with increasing cyanide ion concentration. The drop in extractability of gallium is explained, presumably, not by the effect of the cyanide ion, but by the increase in the alkalinity of the solution following upon increasing KCN concentration, as a result of which gallium partially changes into an anionic form which does not react with thiooxine. Nevertheless, the bulk of the gallium present in solution does pass over into the extract, which indicates that it is impossible to determine indium in the presence of gallium by means of thiooxine.

These experiments show that cyanide ions do not form an appreciably stable complex with indium. But, as the technique described above shows, the experiments on the study of the effect of cyanide on the extractability of indium in a strongly alkaline medium were carried out without tartrate; nevertheless, indium was extracted completely in the form of the compound $In(C_9H_6NS)_3$. This indicates that cyanide ions form some sort of complex of low stability with indium, which prevents formation of indium hydroxide which does not react with thiooxine.

Thus indium can be photometrically determined in the presence of KCN and tartrate, but gallium cannot be determined in this way. In this connection we have examined the effect of thiooxine concentration on the extractability of indium in the presence of 20 ml of 40% KCN solution. The amount of indium taken, and the whole experimental procedure were identical to those described above. Only the concentration of sodium thiooxinate in the test solution was varied from experiment to experiment. These experiments show that five times the theoretical amount of thiooxine necessary for formation of $In(C_9H_6NS)_3$ should be used for ensuring quantitative extraction of indium. Further increases in thiooxine concentration do not affect the extractability of indium.

The sensitivity of the reaction and conformation of solutions of indium thiooxinate to Beer's law. A calibration curve was constructed by introducing 10 ml of 20% sodium tartrate, and 20 ml of 40% KCN solution into a 200 ml separating funnel; these were followed by various amounts of a solution of an indium salt and 1 ml of 1.25% sodium thiooxinate solution, the volume of the aqueous phase being finally made up to 50 ml. The indium thiooxinate was extracted by vigorous shaking for 3 min with 10 ml of toluene. After filtration through a plug of cotton wool, the optical density of the extract was measured in a 1 cm cell on a spectrophotometer at 407 mμ or on a photocolorimeter with a violet filter. When the FEK-N-54 photocolorimeter was used it was found that toluene solutions of indium thiooxinate confirm to Beer's law over the range 5-60 μg indium/ml. When 10 ml of toluene is used for extraction it is possible to determine as little as 0.5 μg indium, with an error of ±10%. The error decreases to 3-4% in the case of larger amounts of indium.

Indium can also be determined in a weakly acid medium at pH 5-6. The extracts obtained in an acetate buffer (without tartrate and cyanide) conform to Beer's law over the same indium concentration range. The curve is, however, somewhat higher since the isoelectric point of thiooxine is located at pH 5.1, and at this point thiooxine exhibits its lowest solubility in water and is most completely extracted with organic solvents so that a continuous supplementary background is created.

Determination of indium in the presence of other elements. In the experiments described below, which were carried out by the method used above for constructing a calibration curve (in an alkaline medium in the presence of cyanide and tartrate), 20 μg of indium was determined against a background of various amounts of foreign elements. The optical density of the toluene extracts was measured on a FEK-N-54 photocolorimeter fitted with a violet filter. The amount of indium to be determined was found from the calibration curve constructed with the aid of pure solutions of indium as described above. The results obtained are given in Table 2. KCN was used for masking Cu, Cd, Ag, Au, Co, Ni, Fe and Pt. Gold must be reduced beforehand with sodium metabisulfite at pH 5-6 to its univalent state, since Au^{III} vigorously oxidizes thiooxine to 8,8'-diquinolyldisulfide. For determination of indium in the presence of gold, 10-20 ml of the acid test solution is neutralized to pH 3-5, 4 ml of a 30% sodium acetate solution is added, followed by 5 ml of 20% sodium metabisulfite and 1 ml of a 1.25% solution of sodium thiooxinate. The procedure outlined above is then followed. It is possible to determine microgram amounts of indium in the presence of 250 mg of gold by this method.

TABLE 2. Determination of Indium in the Presence of Other Elements (20 μg In taken)

Foreign element (Me), mg		Ratio In : Me	In found, μg	Error, %	Foreign element (Me), mg		Ratio In : Me	In found, μg	Error, %
Cu^{2+}	10	1 : 500	20,5	2,5	W^{VI}	1500	1 : 75000	21	5
Cd^{2+}	1	1 : 50	19	—5	Re^{VII}	20	1 : 1000	20	0
Ag^{+}	3000	1 : 150000	20	0	Fe^{2+}	150	1 : 7500	19,5	—2,5
Au^{+}	250	1 : 12500	21	5	Co^{2+}	20	1 : 1000	20,4	2
Ge^{IV}	1200	1 : 60000	19,6	—2	Ni^{2+}	30	1 : 1500	20,5	2,5
Th^{IV}	500	1 : 25000	19,4	—3	Pd^{2+}	50	1 : 2500	20,9	4,5
V^{V}	20	1 : 1000	20	0	Pt^{IV}	100	1 : 5000	20,5	2,5
As^{V}	500	1 : 25000	20,5	2,5	Os^{VIII}	6,2	1 : 310	19,7	—1,5
Cr^{III}	140	1 : 7000	20,8	4	UO_2^{2+}	580	1 : 24000	19	—5
Mo^{VI}	1000	1 : 50000	19,6	—2					

Iron can only be bound as a fairly stable cyanide complex after reducing it to its divalent state with hydroxylamine or ascrobic acid. Other reducing agents (NaH_2PO_2, Na_2SO_3, $Na_2S_2O_4$) do not reduce iron quantitatively to Fe^{2+}, so that iron cannot be complexed completely. Two ml of a freshly prepared 20% solution of ascorbic acid (or hydroxylamine) is added to 10-20 ml of the weakly acid test solution, 2 ml of 20% sodium tartrate solution is then added, and the solution obtained neutralized with alkali to pH 8-9, 20 ml of 40% KCN solution is added and the whole boiled until the color of the solution changes to pure yellow. The procedure outlined above is then followed. Microgram amounts of indium can be determined in the presence of 120 mg iron by this method.

Other elements, in the amounts indicated in Table 1, do not introduce any difficulties into the determination of indium. Neither do any of the elements which do not form sulfides which are stable to the action of water interfere (Al, Zr, Tl, etc.).

Mn, Zn, Hg, Ga, Tl, Sn, Pb, Sb and Bi should be absent.

Anions (Cl^-, Br^-, I^-, F^-, NO_3^-, SO_4^{2-}, CH_3COO^-, ClO_4^-, $B_4O_7^{2-}$, CNS^-, PO_4^{3-}, CO_3^{2-}, $C_2O_4^{2-}$, NO_2^- citrate, tartrate, and cyanide) do not affect the accuracy of indium determination.

SUMMARY

Crystalline gallium $Ga(C_9H_6NS)_3$, indium $In(C_9H_6NS)_3$, and thallium TlC_9H_6NS thiooxinates have been synthesized. It has been established spectrophotometrically that gallium thiooxinate dissociates in organic solvents to form the ion $Ga(C_9H_6NS)_2^+$. Indium thiooxinate tends to dissociate in the same way but to a lesser extent. The values of the molar extinction coefficients of gallium thiooxinate (ϵ = 8400) and indium thiooxinate (ϵ = 11,000), measured

at the absorption maxima of the complexes, also testify to complete dissociation of gallium thiooxinate with formation of the ion $Ga(C_9H_6NS)_2^+$, and partial dissociation of indium thiooxinate with formation of the ion $In(C_9H_6NS)_2^+$. Thallium thiooxinate has a molar extinction coefficient of about 4000, which confirms the composition TlC_9H_6NS.

Indium and thallium thiooxinates have the same composition in solution in organic solvents and in the crystalline state. Gallium thiooxinate is formed at a ratio of Ga : R = 1 : 2, i.e., organic solvents apparently extract a complex of the composition $Ga(C_9H_6NS)_2$ or a basic thiooxinate $Ga(C_9H_6NS)_2OH$.

When ten times the amount of thiooxine theoretically necessary for formation of the thiooxinates is used, gallium is extracted at pH 6.5-10, indium at pH 4-13, and thallium at pH 9-14. Under similar conditions gallium 8-hydroxyquinolate is extracted at pH 3.5-11 and indium 8-hydroxyquinolate at pH 5-13.

A method has been developed for the photometric determination of indium with thiooxine (8-mercaptoquinoline). The method is based on formation of indium thiooxinate $In(C_9H_6NS)_3$ which is extracted with toluene to give a yellow colored solution. The indium complex is extracted at pH 4-12.5. From 0.5 to 60 μg of indium can be determined in 50 ml. The selectivity of the reaction is low in a weakly acid medium. It is possible to mask overwhelming amounts of Cu, Ag, Au, Fe, Co, No, Pb, and Pt by means of potassium cyanide in an alkaline medium. Ge, V, As, Mo, W, Re, U and all those elements which do not form sulfides which are stable in aqueous solution (Al, Zr, Ti, Cr, Th, etc.) do not interfere either. Mn, Zn, Hg, Ga, Tl, Sn, Pb, Sb, and Bi interfere with indium determination. The advantage of the method suggested is the possibility of determining microgram amounts of indium in the presence of overwhelming amounts of silver, gold, palladium, and platinum without preliminary removal of these elements. The thiooxine method for the determination of indium in an alkaline medium in the presence of potassium cyanide is more selective than the 8-hydroxyquinoline method.

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2,7-DICHLOROCHROMOTROPIC ACID – A NEW REAGENT FOR THE PHOTOMETRIC DETERMINATION OF TITANIUM

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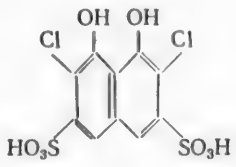
Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 573-577,
September-October, 1961
Original article submitted March 23, 1961

Relatively few good reagents are known for titanium. Arsenazo, thoron, and other reagents give color reactions of low contrast and selectivity with titanium. Reactions based on formation of the bond Ti–O [1] are of the greatest practical importance for titanium. Determination of titanium with hydrogen peroxide [2] is not too sensitive and selective. More sensitive are methods based on the reagents: tairon, sulfosalicylic acid [7-9], salicylic acid [9-11], pyrocatechol [5, 12, 13], ascorbic acid [14-16], diantipyrylmethane [17], salicylhydroxamic acid [18], dihydroxymaleic acid [19] etc. These reagents approximate in sensitivity to chromotropic acid [20] – one of the most sensitive of the readily available reagents for titanium. Chromotropic acid has been used for developing a number of methods of determining [21-26] and detecting [27-33] titanium in various materials, and a considerable amount of work has been devoted to studies of its complexes with titanium [34-38] and other elements [39-43]. Chromotropic acid, however, has serious disadvantages: its solutions darken on standing [21] and this process is accelerated in the presence of copper [36]; it is almost impossible to obtain colorless preparations of the reagent. Browning of aqueous solutions of chromotropic acid is related to its oxidation as a result of the high reactivity of the hydrogen atoms in positions "2" and "7." When the latter are substituted by chlorine or bromine atoms, the reagents obtained are stable to oxidation.

The present article is devoted to a description of a new organic reagent for quadrivalent titanium – 2,7-dichlorochromotropic acid – which has been synthesized by the authors, and to the possibilities of its analytical application.

Dichlorochromotropic acid exists as fine, colorless needles



which are soluble in water and sparingly soluble in ethanol. Its disodium salt crystallizes with two molecules of water; it is less soluble than the free acid, and is readily purified by recrystallization from water.

The absorption curves of solutions of disodium dichlorochromotropate are shown in Fig. 1. Aqueous solutions of this salt are colorless and hardly change at all on storing in direct sunlight. Special experiments devoted to a study of the comparative stability of 0.01 M aqueous solutions of chromotropic and dichlorochromotropic acids to hydrogen peroxide, showed that chromotropic acid darkens 400 times more quickly than dichlorochromotropic acid under such conditions.

Dichlorochromotropic acid interacts, under suitable conditions for each element, to form colored compounds with Ti^{IV} (raspberry), Fe^{III} (green), U^{VI} (brown), $Hg^{II,I}$ (pale light-yellow), Mo^{VI}, W^{VI} (yellow), Cr^{VI} (rose-violet in almost concentrated H_2SO_4), V^{IV} (dark-green). Ce^{IV} and Mn^{VII} oxidize the reagent, as a result of which a yellow color develops.

Under the conditions used for the photometric determination of titanium, dichlorochromotropic acid does not give colors with Ag, Al, Ba, Be, Bi, Ca, Cd, Co^{II}, Cr^{III}, $C^{I,II}$, Fe^{II}, Ga, $Hg^{I,II}$, In, Mg, Mn^{II}, Ni, Pb, Pt^{IV}, Sb^{III}, Se^{VI}, $Sn^{II,IV}$, Sr, Te^{IV}, Th, Tl^{III}, ΣTR, Zn, Zr.

Solutions of titanium compounds have an absorption maximum at 490 mμ. Dichlorochromotropic acid reacts with Ti^{IV} in more acid media than chromotropic acid; the pH values at which the reaction proceeds to 50% extent are 0.7 and 1.8 respectively. The effect of pH on color development is shown in Fig. 2. The sensitivity of dichlorochromotropic acid for titanium at pH 1.0 is 12 times the sensitivity of the hydrogen peroxide reaction, while at pH 2.0 it is 14 times more sensitive. The comparison was made with the sensitivity of the reaction under the conditions used for determination of titanium with hydrogen peroxide [44]. The molar extinction coefficient of solutions of the compound formed between titanium and dichlorochromotropic acid is equal to $1.12 \cdot 10^4$ at pH 2.0, and $0.80 \cdot 10^4$ at pH 1.0 and λ = 490 mμ.

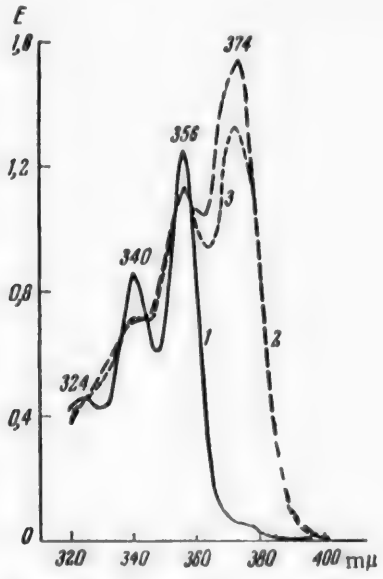


Fig. 1. Absorption curves of $1 \cdot 10^4$ M solutions of disodium dichlorochromotropate. 1) In 0.1 N H_2SO_4 (against H_2O); 2) in 0.1 N NaOH (against 0.1 N NaOH); 3) in H_2O (pH 4.1; against H_2O SF-4 spectrophotometer, 10 mm cell.

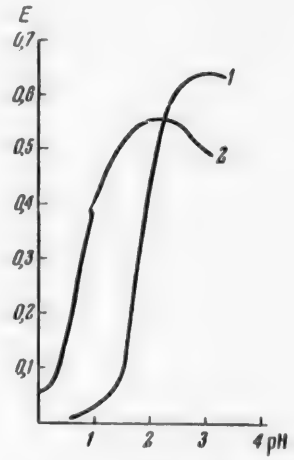


Fig. 2. Effect of pH on the development of color between Ti^{IV} and 1) chromotropic acid (λ = = 450 mμ); 2) dichlorochromotropic acid (λ = 490 mμ); concentrations: reagent, $5 \cdot 10^{-4}$ M; titanium $5 \cdot 10^{-5}$ M; SF-5 spectrophotometer, 10 mm cell.

In $7.5 \cdot 10^{-4}$ M solutions of dichlorochromotropic acid at pH 1.0, using a 10 mm cell and a wavelength of 490 mμ, 0.1 μg Ti/ml gives an extinction of 0.018. For the reagent concentration indicated the calibration line is linear up to a titanium concentration of 4-5 μg/ml. Results of the spectrophotometric determination of titanium in pure solutions are given in the table.

Spectrophotometric Determination of Titanium with Dichlorochromotropic Acid. Reagent Concentration $7.5 \cdot 10^{-4}$ M (volume of solution 10 ml, cell 10 mm, λ = 490 mμ. The optical density was measured relative to a solution of the reagent)

Ti taken, μg	Found			
	pH 1.0 (0.1 N HCl)		pH 2.0 (0.001 N HCl)	
	μg Ti	relative error, %	μg Ti	relative error, %
1	1.05	+5	1.00	0.0
5	5.05	+1	5.00	0.0
25	25.2	+0.8	15.0	0.0
50, 40	50.1	+0.2	40.0	0.0

The reaction is fairly selective at pH 1.0. Under these conditions, U^{VI}, V^{IV}, and $Hg^{II,I}$ do not interfere with titanium determination. Fe^{III}, Cr^{VI}, V^{V}, Mo^{VI}, and W^{VI} interfere strongly. Interference from Fe^{III}, V^{V}, and Cr^{VI} can be removed by reducing them with ascorbic acid, while Mo^{VI} and W^{VI} can be masked with phosphate.

The masking effect of fluorides, phosphates, tartrates, and sodium ethylenediaminetetracetate (EDTA-Na) is shown in Fig. 3. In the case of the reaction of Ti^{IV} with dichlorochromotropic acid, the effect of oxalates is almost analogous to the effect of EDTA-Na. Ascorbic acid in 100-fold excess does not mask Ti^{IV}.

Determination of small amounts of titanium in dilute solutions. In analytical practice, e.g., during hydrochemical studies, it is frequently necessary to determine microgram amounts of elements in very dilute solutions.

In such cases photometric determinations are carried out after preliminary concentration extraction, or after using the new technique of coprecipitation with colorless organic coprecipitants [45]. We also used these techniques for the determination of titanium in dilute solutions. It is known [45, 46] that in order to extract water soluble complex compounds formed with organic reagents containing sulfo groups, it is necessary to add salts of heavy hydrophobic organic cations to the solution. Diphenylguanidine [45, 46] and triphenylguanidine [47] etc., are used for this purpose.

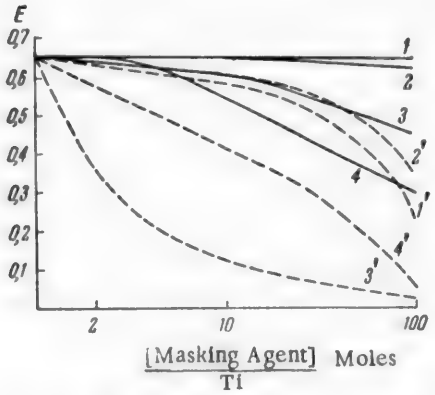


Fig. 3. Effect of tartrates (1), phosphate (2), EDTA-Na (3), and fluorides (4) on the reaction between Ti^{IV} and chromotropic acid (pH 3.0, λ = 450 mμ); and dichlorochromotropic acid)pH 1.0, λ = 490 mμ); concentrations: reagent, $7.5 \cdot 10^{-4}$ M; titanium $5 \cdot 10^{-5}$ M.

We used diphenylguanidine (DPG) and n-butanol for extracting the complex of titanium with dichlorochromotropic acid. It was found that 0.25 μg Ti is almost quantitatively extracted by 3-5 ml of butanol from 25 ml of 0.1 N H_2SO_4. In the butanol medium, just as in an aqueous medium, there is a linear relation between optical density and titanium concentration. In a butanol medium, 0.1 μg Ti/ml in a 10 mm cell at 490 mμ gives an extinction of 0.016.

For extracting titanium from 0.1 N H_2SO_4 at a concentration of 0.01-1 μg Ti/ml in solution, 1.5-2.0 ml of a 0.24% aqueous solution of disodium dichlorochromotropate, and 4 ml of 20% DPG chloride per 25 ml of solution should be added to the solution. At higher titanium dilutions, e.g., at titanium concentrations of the order of 0.001 μg/ml, it is not convenient to use extraction for concentrating the titanium. In such cases it is more convenient to use coprecipitation with colorless coprecipitants: this method gives good results at titanium dilutions down to $1:10^9$ (0.25 μg Ti in 250 ml). The complex of titanium with dichlorochromotropic acid is coprecipitated from 0.1 N H_2SO_4 with precipitates of diphenylguanidine α-anthracenesulfonate. The following procedure is adopted. To 250 ml of test solution which has an acidity of 0.1 N with respect to H_2SO_4, and which has a titanium concentration of 0.001 μgTi/ml or more, is added 4 ml of a 2.4% aqueous solution of disodium dichlorochromotropate and 5 ml of a 1.8% aqueous solution of potassium α-anthracenesulfonate; 6.6 ml of a 20% aqueous solution of diphenylguanidine is then added with stirring. The precipitate which settles out is filtered off through a funnel fitted with a glass filter (No. 3) or through a filter paper, and dissolved in 5 ml of butanol. The optical density of the solution obtained is measured in a 10 mm cell at 490 mμ relative to a blank prepared in parallel. The titanium content is found from a calibration curve.

Other instances of the analytical application of dichlorochromotropic acid. Preliminary experiments have shown that this reagent gives sensitive color reactions with UO_2^{2+}, Fe^{III}, and V^{IV}; and these reactions may be of interest for the photometric determination of these elements. Dichlorochromotropic acid is also of interest for the titration of zirconium, thorium, and other elements when the appropriate metalloindicators are used.

Other examples of the analytical application of dichlorochromotropic acid will be described in future communications.

The synthesis of 2,7-dichlorochromotropic acid has been described elsewhere [48].

SUMMARY

2,7-Dichlorochromotropic acid whose solutions are colorless and stable is suggested as a replacement for unstable chromotropic acid for the photometric determination of titanium. The reagent gives a raspberry color with Ti^{IV}, a green color with Fe^{III}, a brown color with U^{VI}, and a yellow color with Mo^{VI} and W^{VI}; Al, Zr, Mg, and Ca do not give colors with it. At pH 2.0 and at λ = 490 mμ the molar extinction coefficient is $1.12 \cdot 10^4$. Interference from Fe^{III} can be prevented with ascorbic acid, while interference from Mo and W can be prevented with phosphates. In order to determine titanium in solutions in which its concentration is 0.01 μg Ti/ml, its complex with dichlorochromotropic acid is extracted at pH 1 with butanol after addition of diphenylguanidine chloride. At titanium concentrations of 0.001 μg/ml, the titanium complex is first coprecipitated with a colorless organic coprecipitant, by addition of potassium α-anthracenesulfonate and diphenylguanidine chloride. The precipitate formed is filtered off, dissolved in butanol and the optical density of the solution obtained measured at 490 mμ in a 10 mm cell.

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EXTRACTION-PHOTOMETRIC DETERMINATION OF MOLYBDENUM BY MEANS OF 6,7-DIHYDROXY-2,4-DIPHENYLBENZOPYRILIUM CHLORIDE

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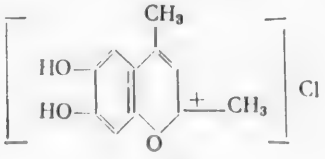
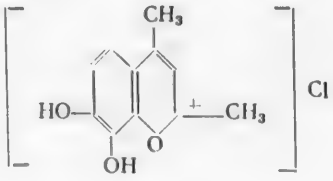
Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 578-584, September-October, 1961
Original article submitted May 12, 1960

Numerous organic materials containing two hydroxy groups in the ortho position to one another in the benzene ring are reagents for sexivalent molybdenum. Examples of such reagents are pyrocatechol, pyrocatecholdisulfonic acid, stilbazo, morin, etc. It has been pointed out [1] that the two ortho arranged hydroxy groups ensure formation of characteristically colored compounds with molybdenum, and also with Ge, Sn^{IV}, Sb, and Zr. Orthodihydroxychromenols, (I-IV) which were recently suggested by Kononenko and Poluektov [2] for the photometric determination of germanium, belong to this group of potential reagents for molybdenum.



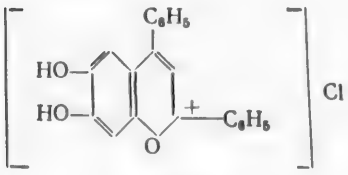
(I)

6,7-dihydroxy-2,4-dimethylbenzopyrilium chloride



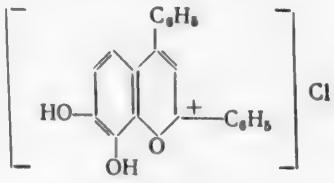
(II)

7,8-dihydroxy-2,4-dimethylbenzopyrilium chloride



(III)

6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride



(IV)

7,8-dihydroxy-2,4-diphenylbenzopyrilium chloride

They contain two ortho hydroxy groups in the benzene ring, and, as one might expect, give colored compounds with sexi- and quinquevalent molybdenum; some of them permit determination of microgram amounts of this element by an extraction-photometric method. The analytical methods which have been developed on the basis of these reagents have, in a number of instances, advantages over current methods.

EXPERIMENTAL

Solutions of the o-dihydroxychromenols* were prepared by dissolving accurately weighed aliquots of the preparations in water or ethanol (the dimethyl derivatives were dissolved in water, while the diphenyl derivatives were dissolved in ethanol). The synthesis and some of the properties of the o-dihydroxychromenols have been described in the article by Kononenko and Poluektov [2].

* The authors would like to thank L. I. Kononenko and N. S. Poluektov who supplied us with the o-dihydroxychromenols.

Standard sodium molybdate solution was prepared by dissolving the pure salt in water; the concentration of the solution was established by means of the 8-hydroxyquinoline method [3]. One ml of solution contained on an average 4.96 mn Mo. This stock solution was diluted to give solutions of the requisite concentration.

Optical density was measured throughout on a SF-4 spectrophotometer using a cell with a path length of 1 cm. pH was measured with a pH-meter using a glass electrode.

DISCUSSION

Kononenko and Poluektov [2] have pointed out that aqueous and aqueous-ethanol solutions of the o-dihydroxychromenols, depending on the pH of the solution, have three colored forms and possess the properties of acid–base indicators.

On adding a dilute solution of sodium molybdate to solutions of o-dihydroxychromenols (I-IV) in a weakly acid medium (pH 2-3) a color change is observed (Table 1), which indicates formation of colored compounds. The latter can be extracted with chloroform and other organic solvents.

TABLE 1. Color Change of Weakly Acid Solutions of the o-Dihydroxychromenols on Adding Sodium Molybdate

Reagent	Color of aqueous solutions, pH 2-3		Color of $CHCl_3$ extracts (aqueous phase with pH 2-3)	
	reagent	molybdenum compound	reagent	molybdenum compound
I	Pale-yellow	Bright-yellow	Pale-yellow	Yellow
II	Lemon-yellow	Orange	Not observable	Not observable
III	Lemon-yellow	Red	Orange	Red
IV	Orange-red	Dirty-green	Violet-blue	Blue

TABLE 2. Molar Extinction Coefficients of Solutions of Molybdenum Compounds with o-Dihydroxychromenols

Reagent	Aqueous solution		Extract in $CHCl_3$	
	pH	E_M	pH	E_M
I	2.45	$3 \cdot 10^4$ (at 432 mμ)	2.2	$4 \cdot 10^4$ (at 470 mμ)
II	3.25	$8 \cdot 10^3$ (at 500 mμ)	–	–
III	2.12	$5 \cdot 10^4$ (at 520 mμ)	1.0	$5 \cdot 10^4$ (at 535 mμ)
IV	2.20	$6 \cdot 10^3$ (at 630 mμ)	–	–

In order to calculate the approximate values of the molar extinction coefficients, optical density measurements were made on solutions of mixtures of sodium molybdate and five times its amount of the o-dihydroxychromenols (excess of the latter cannot be reduced) at the optimum pH of the solutions and at wavelengths corresponding to the absorption maximum; the reference solution was a solution of the reagent with the same concentration and pH (Table 2). Of the four o-dihydroxychromenols studied, 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride which gives an intense red colored compound with molybdate in a weakly acid medium proved to be the most sensitive reagent for molybdenum.

The colored compounds of molybdenum with the dimethyl derivatives of the chromenols are soluble in water, while those with the diphenyl derivatives are insoluble in water and precipitate out; at low concentrations of molybdate a colloidal solution is formed.

Reagents (I-IV) react analogously with a solution of a quinquevalent molybdenum salt.

The effect of pH on formation of the compound of molybdenum with the o-dihydroxychromenols was established. 2.5 ml of a 10^{-3} M solution of the reagent (I) was added to 2.5 ml of a $2 \cdot 10^{-4}$ M solution of sodium molybdate. The final volume was 25 ml, and the pH of the solution was adjusted by addition of hydrochloric acid or sodium

hydroxide, establishment of the requisite pH being controlled by means of a glass electrode. The optical density was measured at 440 mμ relative to water. The results obtained are given in Fig. 1 (curve 1). Experiments were carried out in the same way with solutions of the reagent (I) of equal concentration (Fig. 1, curve 2). The difference curve (Fig. 1, curve 3) shows the relationship between formation of the molybdenum compound and the pH of the solution. The optimum value of the acidity of the solution for color development is found within the narrow pH range 2.5-3. Over this same interval there is a sharp increase in the optical density of a solution of the reagent itself. All this complicates the use of reagent (I) for the photometric determination of molybdenum in aqueous solutions. Similar results were obtained in aqueous solutions with the other o-dihydroxychromenols. In the case of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride the optimum pH of the solutions is 2.

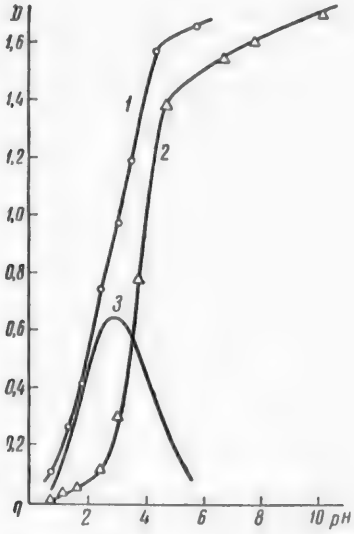


Fig. 1. Effect of pH on the optical density of solutions of the compound of molybdenum with reagent (I). 1) Solution of a mixture of sodium molybdate and reagent (I); 2) solution of the reagent alone (I); 3) difference curve.

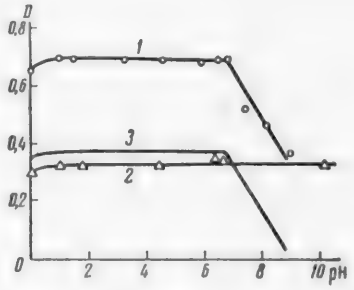


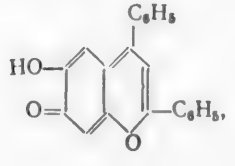
Fig. 2. Effect of the pH of the aqueous phase on the optical density of a chloroform extract of the compound of molybdenum with reagent (III). 1) Extract of a mixture of sodium molybdate and reagent (III); 2) extract of reagent (III); 3) difference between curves 1 and 2.

Determination of molybdenum by means of the o-dihydroxychromenols by measuring the optical density of aqueous solutions is not expedient, since it is necessary to take at least a four-fold excess of reagent over the molybdenum, and the color of the reagent is partially superimposed on the color of the molybdenum compound formed.

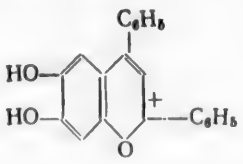
Determination of microgram amounts of molybdenum is best carried out using 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride as the reagent, extracting the molybdenum compound formed with this reagent with chloroform, and measuring the optical density of the extract. This variant of the method possesses a high sensitivity, is readily carried out, and gives completely satisfactory results.

6,7-Dihydroxy-2,4-dimethylbenzopyrilium chloride is less suitable for the extraction photometric determination of molybdenum since the optical density of the chloroform extract in this case is strongly dependent on the pH of the aqueous phase.

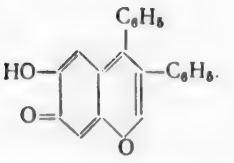
It is interesting to note that a chloroform extract of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride has an orange color, and the optical density of the extract at 535 mμ is independent of the pH of the aqueous phase (Fig. 2, curve 2). It is probable that in this case only undissociated molecules of the orange colored anhydro base are extracted:



during extraction the reagent changes from the ionic form



into the molecular form



pH Range for extraction photometric determination of molybdenum. To determine the optimum value of the pH of the aqueous phase during extraction photometric determination of molybdenum, 0.4 ml of $2 \cdot 10^{-4}$ M sodium molybdate solution and 0.2 ml of a $2 \cdot 10^{-3}$ M solution of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride in alcohol were mixed; dilute HCl or NaOH were then added to adjust the pH to the requisite value and the mixture obtained was diluted with water to 10 ml. Exactly 10.0 ml of $CHCl_3$ was next added from a buret and the whole vigorously shaken for 4 min. After the phases had separated the optical density of the extract was measured at 535 mμ relative to chloroform (Fig. 2, curve 1). The pH of the aqueous solution was controlled by means of a pH-meter with a glass electrode, after extraction. The optical density of an extract of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride at various pH values of the aqueous phase was measured in the same way, but at a constant concentration of the reagent (Fig. 2, curve 2). The difference between curves 1 and 2 is shown by curve 3. It is clear that the optical density of the extract of the molybdenum compound is independent of pH over a large pH range of the solution (1-6.5).

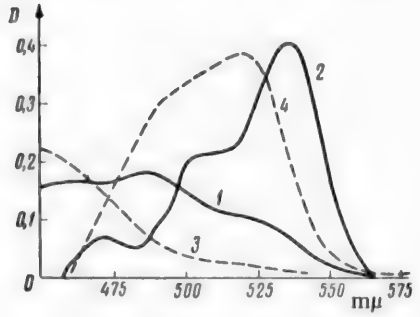


Fig. 3. Absorption curves. 1) $CHCl_3$ extract of reagent (III); 2) extract of the compound of molybdate with reagent (III) (in $CHCl_3$); 3) 50% aqueous-acetone solution of reagent (III); 4) 50% aqueous-acetone solution of the compound of molybdate with reagent (III).

At pH < 1 low results were obtained because of incomplete extraction of molybdenum. At pH higher than 6.5 a sharp decrease in optical density was observed, although, according to published results, it is the molybdate anion MoO_4^{2-} which is mainly present in solution. Probably, the reagent forms a stable compound with the molybdenyl cation MoO_2^{2+}.

The optical properties of solutions of the molybdenum compound. The absorption curve of a $8 \cdot 10^{-6}$ M solution of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride in a 1:1 mixture of water and acetone at pH 2.12 relative to water is shown in Fig. 3 (curve 3). The absorption maximum is located at 450 mμ;* addition of molybdate to the reagent leads to a shift in the maximum toward the higher wavelengths. The absorption curve of the compound of molybdenum with the reagent in 50% acetone has a maximum at 520 mμ (Fig. 3, curve 4). The sodium molybdate and reagent concentrations in this case were $4 \cdot 10^{-5}$ and $8 \cdot 10^{-6}$ M respectively at pH 2.12. The optical density was measured relative to a solution of the reagent with the same concentration. The absorption curve of a chloroform extract of the molybdenum compound has a maximum at 535 mμ (Fig. 3, curve 2). The extract was obtained by the same method as that used in establishing the optimum pH value of the aqueous solution during extraction. The optical density was measured relative to a chloroform extract of the reagent. The chloroform extract has an orange color. There is a diffuse maximum at 485 mμ on the absorption curve of a $8 \cdot 10^{-6}$ M solution of the reagent. An extract of the reagent itself also absorbs light at 535 mμ. Accordingly, during photometric determination of molybdenum, the optical density should be measured relative to an extract of the reagent of the same concentration.

* According to Kononenko and Poluektov's results [2] the absorption maximum of aqueous solutions of the reagent containing 1.0% ethanol and gelatin, is found at about 440 mμ.

The molar extinction coefficient of a chloroform extract of the complex was determined at 535 mμ in the presence of excess of reagent (III) ($1.0 \cdot 10^{-4}$ M) in the aqueous phase. The mean value of seven measurements is $(5.04 \pm 0.03) \cdot 10^4$ (Table 3).

TABLE 3. Molar Extinction Coefficients of Extracts of the Compound of Molybdenum with Reagent (III)

C_{Mo}, M	$D_l^{535} = 1$ cm	E_M^{535}
$0,4 \cdot 10^{-5}$	0,202	$5,0 \cdot 10^4$
1,2	0,585	4,90
1,8	0,903	5,02
0,8	0,410	5,13
0,5	0,250	5,00
1,0	0,520	5,20
1,5	0,750	5,00
	Mean	$(5,04 \pm 0,03) \cdot 10^4$

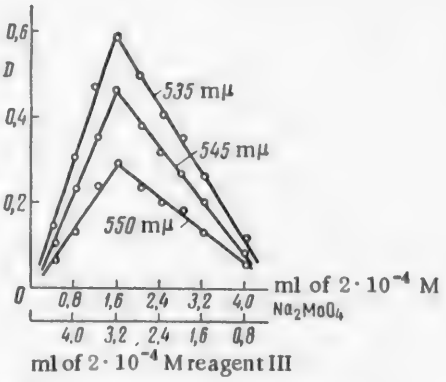


Fig. 4. Molar ratios during interaction of molybdate with reagent (III) as determined by the isomolar series method. The chloroform extract was diluted to 25.0 ml. The optical density was measured relative to chloroform. A correction was applied for the absorption of the reagent.

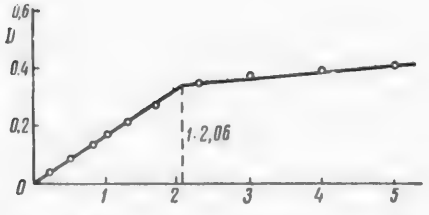
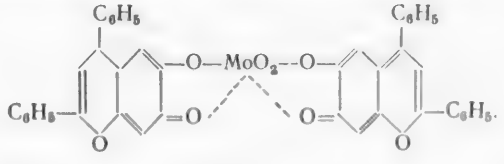


Fig. 5. Molar ratio during interaction of molybdate with reagent (III) as determined by the method of varying the concentration of one of the components. The molar ratio of Mo^{VI} to reagent (III) is plotted along the abscissa.

The composition of the complex. The molar ratio which holds during interaction of molybdenyl ions and 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride was established by the isomolar series method (Fig. 4) and by the method of varying concentrations of one of the components (Fig. 5). The maximum absorption is found at a molar ratio of molybdate to reagent of 1:2 (Fig. 4). In the method in which the concentration of one of the components was varied, during the preparation of series of extracts, the final concentration of sodium molybdate in the aqueous phase was kept constant at $8 \cdot 10^{-6}$ M, while the reagent concentration was varied from $1.6 \cdot 10^{-6}$ to $4 \cdot 10^{-5}$ M. The optical density was measured at 535 mμ relative to an extract of the reagent of the same concentration under the same conditions. A sharp break on the straight line was observed at a molar ratio of molybdate to reagent of 1:2.6 (Fig. 5).

Thus in an acid medium, reagent (III) forms a stable compound, apparently, with the molybdenyl cation:



Determination of molybdenum. 6,7-Dihydroxy-2,4-diphenylbenzopyrilium chloride enabled us to develop an extraction photometric method for determining small amounts of molybdenum in the presence of a series of elements.

It follows from Fig. 5 that during determination of microgram amounts of molybdenum there is no need to add a large excess of reagent. Special experiments showed that it is sufficient to shake for 2-5 min in a 0.1 M HCl medium. The optical density of extracts does not change over a period of several days. The optimum acidity of the aqueous phase is about 0.1 M HCl. Under these conditions sodium ethylenediaminetetracetate (EDTA-Na) masks Fe^{3+} and other ions, and does not interfere with molybdenum determination.

A calibration curve is constructed by introducing 8.5 ml of an almost neutral standard solution of sodium molybdate containing not more than 20 μg molybdenum into a separating funnel; 1 ml of 1 M HCl is then added, followed by exactly 0.5 ml of a $2 \cdot 10^{-3}$ M ethanolic solution of 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride measured out with a pipet. Exactly 10.0 ml of chloroform measured out of a buret is added to the mixture obtained, and the contents of the funnel are vigorously shaken for 3-5 min. After the phases have separated out the orange colored organic phase is isolated (if a turbidity should appear the phase is allowed to stand for the solution to become clear) and its optical density measured at 535 mμ relative to an extract prepared under the same conditions using the same amounts of reagent, but with no molybdenum. Extracts conform to Beer's law (Fig. 6). The sensitivity for molybdenum determination is 0.01 μg Mo/ml.

TABLE 4. Photometric Determination of Molybdenum in the Presence of Foreign Elements

Foreign elements (Me), mg	Ratio Mo:Me	Mo, μg		
		taken	found	error
0,12 Ni ($NiSO_4 \cdot 5H_2O$)	1 : 12	9,5	9,5	0
0,24 Ni	1 : 24	9,5	9,7	+0,2
1,2 Co ($Co(NO_3)_2 \cdot 6H_2O$)	1 : 120	9,5	9,5	0
0,4 Ca ($CaCl_2 \cdot 6H_2O$)	1 : 40	9,5	9,5	0
1,3 Zn ($Zn(NO_3)_2 \cdot 4H_2O$)	1 : 130	9,5	9,6	+0,1
0,06 Cu ($CuSO_4 \cdot 5H_2O$)	1 : 6	9,5	9,6	+0,1
0,12 Cu	1 : 12	9,5	9,8	+0,3
0,1 Cr ($Cr(NO_3)_3 \cdot 6H_2O$)	1 : 10	9,5	9,0	−0,5
0,21 Cr »	1 : 22	9,5	9,5	0
0,55 Mn ($MnCl_2 \cdot 4H_2O$)	1 : 58	9,5	9,6	+0,1
50 50 EDTA-Na	1 : 5000	9,5	9,5	0
100 »	1 : 10 000	9,5	9,5	0
50 Tartaric acid	1 : 5000	9,5	9,6	+0,1
100 » »	1 : 10 000	9,5	9,0	−0,5
2,1 Bi ($Bi(NO_3)_3 \cdot 5H_2O$)*	1 : 210	19,0	19,2	+0,2
0,04 Ti ($TiO(SO_4)_2$)*	1 : 0,4	9,5	9,4	−0,1
0,04 Ti ($TiO(SO_4)_2$)*	1 : 2,1	19,0	19,2	+0,2
0,07 Ti ($TiO(SO_4)_2$)*	1 : 7	9,5	12,6	+3,1
1,1 Fe ($FeCl_3 \cdot 6H_2O$)*	1 : 58	19,0	19,0	0
5,6 Fe ($FeCl_3 \cdot 6H_2O$)*	1 : 560	9,5	9,6	+0,1
33,6 Fe ($FeCl_3 \cdot 6H_2O$)**	1 : 3530	9,5	9,1	−0,4

* In the presence of 1 ml of 5% EDTA-Na solution.

** 1.2 ml of 5% EDTA-Na solution was added per 10 mg Fe.

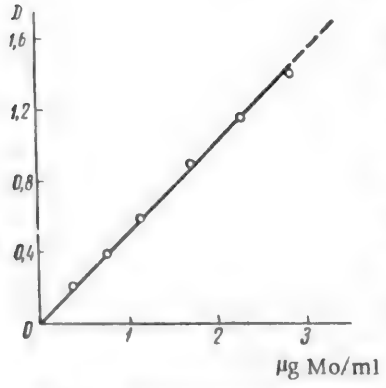


Fig. 6. Calibration curve.

Molybdenum was determined in synthetic mixtures using the same conditions as those employed for constructing a calibration curve, except that before adding hydrochloric acid, the pH of the solution was adjusted to about 2 using universal indicator paper. The results obtained are given in Table 4. Nickel, cobalt, calcium, zinc, copper, divalent manganese, trivalent chromium, EDTA-Na, and tartaric acid do not interfere with molybdenum determination. When EDTA-Na is present, bismuth and even large amounts of trivalent iron, do not interfere with molybdenum determination either. The acidity of the solution must be adjusted accurately in the presence of iron: EDTA-Na is first added to the acid solution (pH about 2), HCl is then added in an amount calculated to ensure that hydrolysis of the iron salt and formation of a compound of sexivalent molybdenum with EDTA-Na (which is formed at pH 4-5) do not occur. Trivalent iron is completely masked by EDTA-Na at pH 1 and does not interfere with determination; under these conditions a precipitate of ethylenediaminetetracetic acid may settle out (particularly in the presence of large amounts of EDTA-Na), but this does not interfere with the determination. Tungsten interferes with molybdenum determination.

Determination of molybdenum in steel is carried out as follows. An aliquot of steel (about 0.1 g) is dissolved in a mixture of 5 ml HNO_3 (1 : 1) and 5 ml H_2SO_4 (1 : 1) contained in a 100 ml beaker, and the solution evaporated to the appearance of white fumes of H_2SO_4. If the steel should not dissolve completely, a few ml of HCl (1 : 1) is

added and the liquid evaporated to dryness; this operation is repeated several times until solution is complete. After cooling, 20 ml of water is added and the liquid heated until the salts have dissolved. The insoluble silica is filtered off through a filter paper, the filter paper plus insoluble residue is washed several times with the minimum amount of water, and the filtrate collected in a 50 ml standard flask. After cooling, the filtrate is diluted to the mark with water, a suitable aliquot of this solution is pipetted into a separating funnel, water is added and the pH carefully adjusted to about 2 (using universal indicator paper) in order to avoid hydrolysis of the iron salts. One ml of a 5% solution of EDTA-Na is then added (for high iron contents, 1.2 ml of the 5% EDTA-Na solution is added per 10 mg iron). One ml of 1 N HCl and 0.5 ml of a $2 \cdot 10^{-3}$ N solution of the reagent are added and the solution made up to 10 ml with water. The procedure used for constructing the calibration curve is then followed. The amount of molybdenum is found from the calibration curve.

TABLE 5. Determination of the Molybdenum Content of Standard Steel Sample No. 31 b. (0.27% Mo). 0.44% C, 0.365% Mn, 0.275% Si, 0.017% S, 0.023% P, 1.24% Cr, 3.40% Ni

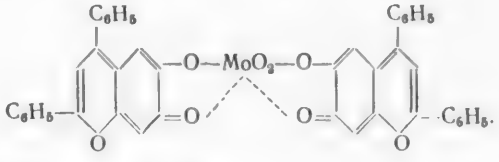
Sample	Mo found, %	Error
1	0.25	−0.02
	0.26	−0.01
2	0.27	0
	0.26	−0.01
3	0.27	0

Satisfactory results were obtained during determination of molybdenum in standard steel, sample No. 31 b (Table 5).

SUMMARY

Of four dihydroxychromenols studied (6,7-dihydroxy-2,4-dimethylbenzopyrilium chloride, 7,8-dihydroxy-2,4-dimethylbenzopyrilium chloride, 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride, and 7,8-dihydroxy-2,4-diphenylbenzopyrilium chloride) as potential reagents for sexivalent molybdenum, 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride gave the best results.

The composition of the compound formed between molybdenum and 6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride has been established:



The molar extinction coefficient is $5.04 \pm 0.03 \cdot 10^4$.

An extraction photometric method has been developed for the determination of molybdenum in steels. The sensitivity of the method is 0.01 μg Mo/ml. The method permits determination of microgram amounts of molybdenum in the presence of nickel, cobalt, calcium, zinc, copper, manganese, and chromium. Bismuth and large amounts of iron do not interfere when sodium ethylenediaminetetracetate is present. Tungsten interferes.

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RESEARCH IN THE ANALYTICAL CHEMISTRY OF URANIUM

COMMUNICATION 4.* PHOTOMETRIC DETERMINATION OF URANIUM BY MEANS OF ARSENAZO I AFTER SEPARATION OF URANIUM FROM IMPURITIES BY MEANS OF THE ANION EXCHANGE RESIN ÉDÉ-10P

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 585-587, September-October, 1961
Original article submitted May 24, 1961

A fairly large amount of work has been devoted to studying the sorption of uranium with anion exchange resins from various media. Some of the results obtained have already found practical application. The most interesting methods are those based on extraction of uranium from sulfuric acid media with strongly basic anion exchange resins. In sulfuric acid solutions, uranium, in practice, forms only one complex with the ratio $UO_2^{2+} : SO_4^{2-} = 1:1$, which is not charged [1-2]. Nevertheless, uranium is readily sorbed by anion exchange resins; this is only possible under conditions in which it is found in solution in the form of an anion. According to Arden, Wood [3] and Miller [4] a negatively charged uranium complex is formed during sorption on the resin surface. One or two SO_4^{2-} ions from the resin add on to the UO_2SO_4 complex and give it a negative charge. The sorption mechanism can be expressed by the following equation:

$$2R_2SO_4 + UO_2SO_4 = R_4[UO_2(SO_4)_4].$$

The capacity of anion exchange resins with respect to uranium decreases with increasing SO_4^{2-} ion concentration and with the acidity of the solution [5]. The latter can be explained by the increase in HSO_4^- ions in solution and on the resin, which prevents formation of anionic complexes of uranium [6]. Articles have been published on the use of the following strongly basic anion exchange resins for the extraction of uranium: Amberlite IRA 400 [7], Dowex 1 [8], and Dowex 2 [9].

The aim of the work described here was to study the application of the Russian anion exchange resin ÉDÉ -10P for extracting uranium from ores and processed products of these ores, with subsequent determination of uranium by means of Arsenazo I. The work reduced to establishing the optimum conditions for selective sorption of uranium from sulfuric acid solutions and for its complete desorption from the resin.

Five-seven ml of resin with a particle size of 0.2-0.4 mm was introduced into a column 10 mm in diameter and was washed with 10% hydrochloric acid until the eluate gave a negative reaction for trivalent iron with potassium thiocyanate. The resin was then converted into the SO_4 form by washing it with 5% ammonium sulfate with a pH of 1-1.5 until the pH of the liquid issuing from the column was equal to the pH of the solution passed into it. One M $HClO_4$ was used initially for eluting uranium.

Uranium is sorbed quantitatively at pH 0.5-3.5 on passing a solution through the column at the maximum possible rate of 4-5 ml/min. Uranium is eluted completely with 100 ml of perchloric acid solution passed through the column at the rate of 2-2.5 ml/min.

Since perchloric acid is not always available, an attempt was made to replace it by a mixture of nitric acid and ammonium nitrate. Uranium elution curves obtained on using such mixtures, with varying composition, are shown in Figs. 1 and 2. It is clear that the eluting action of the mixture is determined, in the main, by the nitrate ion concentration. The optimum nitrate ion concentration appears to be 1 M. Experiments showed that the most effective mixture is one which is 3% with respect to ammonium nitrate and 5% with respect to nitric acid. One-

* For communication 3 see [10].

hundred ml of such a solution passed through the column at the rate of 2.0-2.5 ml/min is sufficient for eluting 2 mg uranium.

The effect of various cations and anions on the sorption of uranium and its subsequent photometric determination with arsenazo I has been studied. It was found that sexivalent molybdenum, although it is sorbed with the uranium, does not interfere with its subsequent determination with arsenazo I, and can therefore be present in appreciable amounts. In the presence of quinquevalent vanadium which interferes with the determination of uranium with arsenazo I, sorption of the uranium should be carried out at pH values ≤ 1, or a reducing agent should be added to the solution. We used a saturated solution of hydrazine sulfate as a reducing agent; when this is done sorption of vanadium only starts at pH ≥ 2.7.

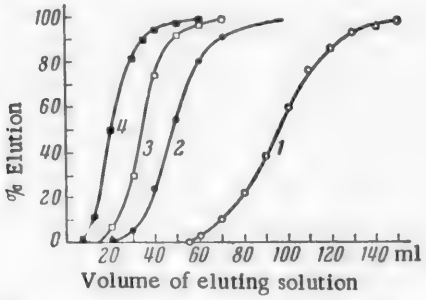

Fig. 1. Elution curves of uranium from the resin ÉDÉ-10P with 3% ammonium nitrate solution, as a function of the HNO_3 content of the solution. The figures on the curves relate respectively to: 1) 1; 2) 3; 3) 5; 4) 10 ml of concentrated HNO_3 in 100 ml of solution.

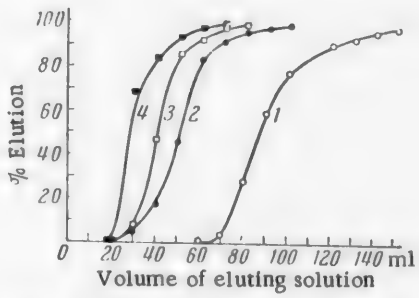

Fig. 2. Elution curves of uranium from the resin ÉDÉ-10P with 3% nitric acid solution, as a function of the NH_4NO_3 content of the solution. The figures on the curves relate respectively to: 1) 1; 2) 3; 3) 5; 4) 10 g of NH_4NO_3 in 100 ml of solution.

Determination of Uranium in Ore Standards

Sample No.	Uranium content, %		No. of determinations	Sample No.	Uranium content, %		No. of determinations
	specified content	by the suggested method			specified content	by the suggested method	
1	0,103±0,002	0,102±0,002	24	6	2,48 ±0,04	2,47 ±0,01	10
2	0,220±0,010	0,217±0,004	9	7	0,059 ±0,004	0,058 ±0,001	14
3	0,530±0,009	0,538±0,004	16	8	0,070 ±0,001	0,070 ±0,001	8
4	0,092±0,008	0,093±0,003	10	9	0,563 ±0,011	0,561 ±0,009	10
5	0,220±0,010	0,211±0,001	8	10	0,0725±0,0004	0,0710±0,001	14

Phosphate ions interfere with the photometric determination of uranium; they are not held firmly by the resin, however, and can be readily removed from the column by eluting the latter with 150-200 ml of ammonium sulfate with pH 0.5-1. When samples contain large amounts of phosphorus, uranium is sorbed at pH 0.5, otherwise a precipitate of uranium forms on establishing the medium. A pH of about 0.5 is also necessary during sorption of uranium from solutions containing titanium. At higher pH values Ti hydrolyzes in the column and interferes with subsequent determination of uranium.

Interference from Cl^- and excess SO_4^{2-} on sorption of uranium was not detected even a molar ratios of 1:15,000 and 1:400,000 respectively. Iron and copper are quantitatively separated from uranium on eluting the column with 150-200 ml of 5% ammonium sulfate solution. Completeness of separation from these elements was checked by testing the eluate for Fe^{III} potassium thiocyanate.

On the basis of the work carried out the following method is suggested for determination of uranium in ores.

EXPERIMENTAL

A 0.5 g aliquot of ore (for uranium contents of 0.01-0.1%) is decomposed with hydrochloric acid and hydrogen peroxide. As soon as only 2-3 ml of liquid remains in the flask it is cooled, 5-7 ml of concentrated sulfuric acid is

added and the liquid evaporated to a volume of 1-2 ml. Evaporation to dryness is not recommended since in such cases low results are obtained, particularly in the presence of phosphorus. Twenty-twenty-five ml of water is added and the liquid boiled for 5-7 min under a watch glass; the insoluble residue is filtered off and the filtrate diluted to 70-80 ml.

When the sample contains vanadium, 2-5 ml of a saturated hydrazine sulfate solution is added to the filtrate obtained and the pH adjusted to 1.0-1.5 by means of ammonia. When a sample contains a large amount of phosphorus and titanium, the pH of the solution should be adjusted to 0.5.

The requisite pH value is established using methyl violet as external indicator (first color change from yellow to green at pH 0.5; second color change from green to blue at pH 1.0-1.5).

The original solution prepared in this way is passed through a column at the rate of 4-5 ml/min.

The column is next washed with 5% ammonium sulfate solution with pH 1-1.5 until the eluate gives a negative reaction for Fe^{III} with potassium thiocyanate, or a negative reaction for PO_4^{3-} with molybdenum solution; the uranium is then desorbed by passing 100 ml of a solution which is 3% with respect to NH_4NO_3 and 5% with respect to HNO_3, through the column. The eluate issuing from the column at this stage is collected in a 100 ml standard flask and the uranium content of this solution determined on an aliquot by means of arsenazo I as described earlier [10]. The column is restored to its operating condition by eluting it with 50-70 ml of a 5% ammonium sulfate solution.

Results for the determination of uranium in a series of ore standards are given in the table. The method is very simple to carry out; no expensive reagents are required. Resin ÉDÉ-10P is characterized by its high mechanical stability and by its resistance to various types of chemical action; we were able to work with one lot of resin for 18 months. Ten to fifteen determinations can be carried out in 10 hr.

SUMMARY

A method has been developed for the photometric determination of uranium in ores by means of arsenazo I after preliminary removal of uranium from impurities with the anion exchange resin ÉDÉ-10P.

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SEPARATION OF RHENIUM AND MOLYBDENUM BY COPRECIPITATION OF THE LATTER WITH FERRIC HYDROXIDE

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 588-591, September-October, 1961
Original article submitted January 19, 1960

Rhenium and molybdenum are separated most often by extraction, by chromatographic methods, by precipitation of certain sparingly soluble compounds, and by distillation of rhenium on heating the solution [1]. These methods differ very much from each other in the efficiency of separation. For separating small amounts of septivalent rhenium and sexivalent molybdenum we have used coprecipitation of the latter with ferric hydroxide. Coprecipitation of perrhenate ions with ferric hydroxide does not exceed a few percent at low rhenium contents and when large amounts of carrier are used [2]. These results were confirmed again under the conditions used for separating rhenium and molybdenum.

First of all we studied the behavior of rhenium and molybdenum, taken separately, during precipitation of ferric hydroxide, and then precipitated the carrier in the presence of perrhenate and molybdate ions. The amount of rhenium remaining in solution and entrained by the precipitate was controlled by means of the radioactive isotope Re^{186}, whose activity was measured with a special quartz cell on a B-2 setup described earlier [3]. In some instances rhenium was determined photometrically by the thiocyanate method. The amount of molybdenum in solution and in the precipitate was determined by the thiocyanate method on a FÉK-N-57 microphotocolorimeter fitted with a No. 3 filter (maximum transmission at 453 mμ). A No. 2 filter with maximum transmission at 413 mμ (Fig. 1) can be used for rhenium determination.

Molybdenum was determined by the same method in all experiments [4]. About 7 ml of an acid mixture (725 ml water, 225 ml H_2SO_4, and 50 ml HCl), 3 ml of a 25% solution of potassium thiocyanate, and 0.5 ml of 10% $SnCl_2 \cdot 2H_2O$ or water were added to the molybdenum containing solution and the volume made up to 25 ml. After mixing, the solution was poured into a cell and its optical density measured; the latter was always measured after the same time interval after addition of the $SnCl_2 \cdot 2H_2O$, since the color intensity changes slightly (curves 4 and 5 in Fig. 1) with time. Special experiments showed that the optical density of solutions of the thiocyanate compound of molybdenum decreases more rapidly the greater the amount of $SnCl_2$.

Coprecipitation was studied under the following conditions: volume of solution 20.0 ml; amount of carrier 0.2 mg at of iron (10.2 mg Fe); NH_4Cl concentration, 1 M; temperature 17°; contact time of solution with precipitate 10-30 min. Ferric hydroxide was precipitated by addition of alkali (potassium hydroxide, ammonia, pyridine) to an acid solution containing iron chloride, molybdate, and perrhenate. The precipitate was separated from the solution by centrifuging. After removal of the precipitate, all the solution was placed in the cell in which the radioactivity of rhenium was measured; subsequently, using a LP-5 pH-meter the pH of the solution was determined. The precipitate was dissolved in 2 ml of 2 N hydrochloric acid; this solution was poured into a beaker containing 10 ml of 0.8 N potassium hydroxide. After centrifuging, the solution was diluted to 20 ml and the molybdenum determined on an aliquot by the thiocyanate method. Under these conditions no coprecipitation of molybdenum with ferric hydroxide was observed.

The amount of solution lost in impregnating the precipitate and remaining on the beaker walls and the centrifuge tubes amounts to about 3-4% of the original volume of solution (20 ml) in the case of 10 mg of iron.

During a study of the coprecipitation of small amounts of rhenium (from 0.2 to 100 μg) it was found that under the experimental conditions used (pH from 5 to 10; NH_4Cl concentration, 1 N) no coprecipitation of rhenium with ferric hydroxide is observed, i.e., the extent of coprecipitation for the most part is zero, and does not exceed 2-3%

of the original amount of rhenium in individual cases, this being approximately equal to the experimental error. Coprecipitation of 1 mg of molybdenum with ferric hydroxide amounts over a certain pH range to 100% and decreased to zero on increasing the pH further (Fig. 2). During precipitation of the carrier in the presence of molybdenum and rhenium, the ratio between rhenium and molybdenum was varied from 1:10 (1 mg Mo: 100 μg Re) to 1:5,000 (1 mg Mo: 2 μg Re). Determination of rhenium and molybdenum in the precipitate of the carrier by Sandell's method [5], which consists in separating Mo and Re by ether extraction of hydrochloric acid solutions of the thiocyanate complex of molybdenum in the presence of mercury, and photometric determination of Re and Mo, showed that that up to 15% of the rhenium taken was present in solution, while the use of the radioactive isotope Re^{186} indicated that the precipitate only contained 2-3% of the rhenium, the latter coming from the solution impregnating the precipitate. Apparently, the extraction method described is not good enough to ensure complete extraction of molybdenum, and therefore leads to errors in rhenium determination.

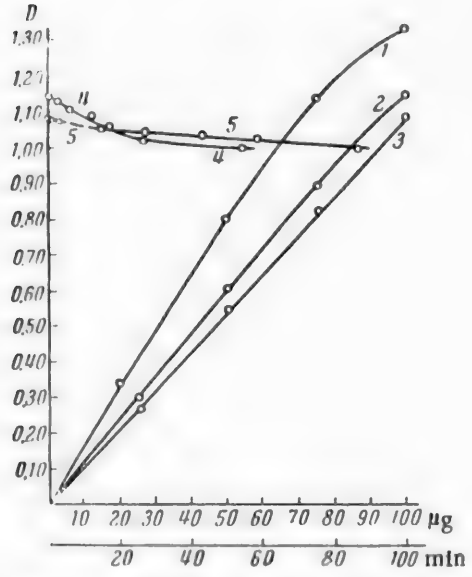

Fig. 1. Calibration curves for rhenium and molybdenum. Change in optical density of solution with time. 1) Re, filter No. 2; 2) Re, filter No. 3; 3) Mo, filter No. 3; 4) and 5) time plotted along the abscissa, Re (4) and Mo (5) in solution.

Results of the study of separating molybdenum and rhenium are given in the table.

During coprecipitation of 1 mg of molybdenum with 0.1 mg atom of iron, incomplete entrainment of the molybdenum by the precipitate occurs (about 94%) at pH 4-5. Presumably, molybdenum enters into the composition of the precipitate in the form of dimeric or polymeric ions, since precipitation is carried out from weakly acid solution. If it is assumed that the precipitate contains ferric hydroxide and normal ferric molybdate, then the composition of the precipitate can be written as $15Fe(OH)_3 \cdot Fe_2(MoO_4)_3$. It can be assumed therefore that the solid phase consists mainly of the carrier—ferric hydroxide — with which the molybdenum is coprecipitated. Complete coprecipitation of 1 mg of molybdenum with ferric hydroxide occurs when the amount of carrier used is greater than 0.1 mg at; 0.2 mg at. of iron is quite sufficient for this purpose. On the basis of the results given in Fig. 2 and in the table, one can make the following conclusions regarding the separation of molybdenum and rhenium by coprecipitation of molybdenum with ferric hydroxide: perrhenate ions, even at low concentrations (from $5 \cdot 10^{-8}$ to $2.7 \cdot 10^{-5}$ g. ion/liter) are hardly coprecipitated at all with ferric hydroxide; 1 mg of molybdenum is completely coprecipitated with 0.2 mg at of iron precipitated as its hydroxide at pH values for incipient coagulation up to 7.5 [7]; on increasing the pH further to 10.5 coprecipitation of molybdenum drops to 0; changes in ammonium chloride concentration from 0.2 to 2 M have no effect on coprecipitation of molybdenum with ferric hydroxide; variations in the contact time of precipitate with solution from 1-2 m to 30 min do not affect the extent to which molybenum is coprecipitated with the carrier.

Separation of Mo and Re by Coprecipitation of Mo with Ferric Hydroxide

Expt. No.	pH	NH_4Cl concentration M	Rhenium taken μg	Rhenium taken cpm	Rhenium found in solution cpm	Rhenium found in solution μg	Rhenium Loss, %	Rhenium Coprecipitated, %	Molybdenum taken μg	Molybdenum found in the precipitate D	Molybdenum found in the precipitate μg	Molybdenum Coprecipitated, %
1	4,98	1	10	3100±16	3026±16	9,76	3	0	1000	1,09	1020	102
2*	5,48	1	10	3040±16	2972±16	9,72	3	0	1000	1,07	1000	100
3	6,12	1	10	3050±16	2930±16	9,61	3	1	1000	1,07	1000	100
4	9,10	1	10	2643±14	2510±14	9,58	3	1,2	1000	0,385	350	35
5*	5,52	2	10	1390±10	1332±10	9,58	3	1,2	1000	1,06	990	99
6*	5,30	0,2	10	1423±12	1390±12	9,70	3	0	1000	1,06	990	99
7*	5,51	1	0,2	461±3	416±5	0,187	3	3,5	1000	1,08	1020	102
8	8,30	1	0,2	455±5	422±5	0,136	3	4	1000	0,75	685	68,5
9												

* In these experiments ferric hydroxide was precipitated by dropwise addition of 0.08 ml of pyridine until coagulation of the precipitate.

Accordingly, the following technique can be recommended for separating and determining small amounts of rhenium and molybdenum: to a hydrochloric acid solution containing rhenium and molybdenum in the highest oxidized form is added ferric chloride at the rate of about 10 mg iron per mg molybdenum; this is followed by ammonium chloride, and then pyridine or ammonia dropwise until the NH_4Cl concentration lies within the limits 0.2-2 M and until the ferric hydroxide is precipitated and coagulated, but not enough to bring the pH above 7. The precipitate which contains all the molybdenum is separated from the solution in which the rhenium is determined by the thiocyanate method. The precipitate is dissolved in hydrochloric acid and this solution is poured into excess alkali; during this stage all the molybdenum dissolves. After removal of the hydroxide by centrifuging, molybdenum is determined in the solution.

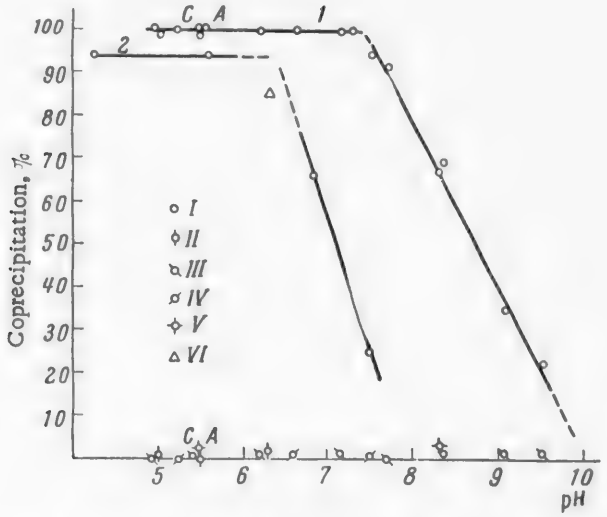

Fig. 2. Coprecipitation of molybdenum and rhenium with ferric hydroxide. 1) Coprecipitation of Mo (0.2 mg at. Fe); 2) ditto (0.2 mg at. Fe; I) Mo = 1 mg; II) Re = 1 μg; III) Re = 10 μg; IV) Re = 100 μg; V) Re = 0.2 μg; VI) Mo = 2 mg; Fe = 0.2 mg at. Points A and C, precipitation with pyridine.

The method suggested is very simple and is applicable to a wide range of molybdenum to rhenium ratios; their separation is complete. The whole operation can be carried out in 10-15 min.

A similar separation method can, as special experiments showed, be applied to the separation of tungsten and rhenium.

SUMMARY

Perrhenate ions are hardly coprecipitated at all with ferric hydroxide under varying conditions. Coprecipitation of molybdenum with ferric hydroxide amounts to 100% over a certain pH range, but can drop to 0.

A simple and rapid method based on coprecipitation of molybdenum with ferric hydroxide at pH < 7.5 is suggested for separating molybdenum and rhenium.

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THE USE OF HYDROXY ACIDS IN POLAROGRAPHIC ANALYSIS

COMMUNICATION 2. DETERMINATION OF MANGANESE IN A SULFOSALICYLATE MEDIUM*

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 592-595,
September-October, 1961
Original article submitted May 20, 1960

The polarographic behavior of many ions in solutions of lactates, malates, and salicylates [1] was the subject of an earlier communication. In order to study the complex forming properties of materials of the given type further, we chose sulfosalicylic acid and its disodium salt, which have hitherto been mainly used during photometric determinations [2, 3]. Complexes of sulfosalicylic acid with cadmium, gallium, iron, titanium, nickel, and manganese have been studied polarographically [4-7]. The results obtained, however, have not been used for analytical purposes.

The present article is devoted to the results of a study of sulfosalicylic acid or its disodium salt as supporting electrolytes; the purpose of the study was to establish the possibility of determining certain ions, in particular, in a alkali media. The most interesting of the restults obtained was the polarographic behavior of the complex of divalent manganese, whose reduction wave was used for its determination in mineral raw material.

EXPERIMENTAL

Sodium sulfosalicylate (0.4 M) solution and 1 M ammonium sulfosalicylate solution were prepared by mixing equivalent amounts of sulfosalicylic acid with NaOH and NH_4OH. The pH of the solutions of the sulfosalicylates was adjusted to a value dependent on the buffer used (Clark and Lebs or borate buffer) by addition of sodium hydroxide or ammonia until the requisite value was obtained, after addition of the salts of test elements.

Polarographic curves were recorded on a V. 301 Heyrovsky polarograph with a 30 galvanometer, using a Calousek cell fitted with a saturated calomel electrode.

Results. Results of the polarographic behavior of individual ions are given in the table. On the basis of preliminary experiments it was established that, from a practical point of view, the most interesting feature is the polarographic behavior of manganese. Divalent manganese in a medium of 0.4 M sodium sulfosalicylate at pH 8-9 gives a colorless complex, as a result of the depolarization of which there appears a wave with a diffusion character at negative potentials (at approximately −0.80 v). On increasing the alkalinity of the solution by addition of sodium hydroxide, gradual oxidation of the divalent manganese complex by atmospheric oxygen to a trivalent manganese complex commences and the solution acquires an olive-brown color. The oxidation rate (followed polarographically) increases on increasing the pH and reaches a maximum at a concentration of 0.1 M NaOH and 0.4 M sodium sulfosalicylate. At higher alkali concentrations precipitation of manganese commences, probably as its hydroxide.

Oxidation of the divalent manganese complex by atmospheric oxygen is manifested polarographically by the appearance of a developed reduction wave with a very positive potential in the range + 0.02 v to −0.17 v (saturated calomel electrode). With increasing alkalinity of the solution the half-wave potential shifts to more negative values.

On increasing the sodium sulfosalicylate concentration, while keeping the sodium hydroxide concentration constant ($5 \cdot 10^{-2}$ M), the half-wave potential hardly changes at all, while the wave height increases. At sodium sulfosalicylate concentrations less than $5 \cdot 10^{-2}$ M (NaOH concentration = $5 \cdot 10^{-2}$ M) a precipitate is formed. It follows therefore that the most suitable electrolyte is a solution of $5 \cdot 10^{-2}$ M NaOH and $4 \cdot 10^{-1}$ M sodium sulfosalicylate. In this medium the half-wave potential of the trivalent manganese complex is equal to −0.14 v (saturated calomel electrode). The diffusion character of the wave is confirmed by the linear relationship between the value of the diffusion current and the height of the mercury reservoir, and also between the value of the diffusion current and the

* Communication 1, see [1].

manganese concentration over the range $1 \cdot 10^{-3} - 1 \cdot 10^{-4}$ M. In this medium quantitative oxidation of divalent manganese is complete within only 3 min as a result of the action of air on the solution. The wave height does not change further even under the continued effect of air; it does not matter therefore how long the solution remains in air after it has been oxidized. No maximum appears on the curve.

Half-wave Potentials of Certain Ions in Sodium and Ammonium Sulfosalicylate

Ion	Media			
	sodium sulfosalicylate		ammonium sulfosalicylate	
	pH 6	pH 8	pH 13	pH 14
Fe^{2+}	a—1,36	a—0,70	e	e
Fe^{3+}	e	a—1,02	a—1,08	a—0,69
Co^{2+}	a—1,32	b—1,46	e	a—1,34
Ni^{2+}	b—1,04	a—1,07	e	b—1,10
Mo^{6+}	g—0,45a—0,65	e	e	e
Ti^{4+}	b—0,80	c—1,26	a—0,74	e
Ge^{4+}	a—1,36	b—1,44	b—1,55	b—1,38
W^{6+}	g—1,35a—1,44	e	e	f
Pd^{2+}	h—0,51	h—0,56	h—0,58	d
Sn^{4+}	b—1,29	c—1,44	g—1,41a—1,62	b—1,38
Sb^{3+}	b—0,63	b—0,72	a—0,75	d
As^{3+}	c—1,38	b—1,67	e	g—1,59
Sb^{5+}	d	a—0,78	b—0,84	b—0,75
Cd^{2+}	c—0,55	b—0,58	a—0,68	a—0,79
Cu^{2+}	a—0,14	b—0,33	b—0,39	g—0,16a—0,46
Tl^{+}	b—0,42	e—0,42	e—0,37	b—0,32
Zn^{2+}	e	g—1,18;—1,32	g—1,41;—1,57	a—1,30
V^{5+}	e	e	e	b—1,13
Mn^{2+}	e	c—0,83	a (Mn^{III})—0,14	a—1,70
UO^{2+}	e	a—0,55	a—0,60	b—0,60
Cr^{6+}	e	c—0,32	a—0,81	b—0,28
Sn^{2+}	e	e	e	e
As^{5+}	e	e	e	e
In^{3+}	e	e	e	e
Ce^{3+}	e	e	e	e
Ce^{4+}	e	e	e	e
Th^{4+}	e	e	e	e

a) Good wave with a diffusion character, suitable for analytical use; b) clearly defined wave with a diffusion character; c) wave which is difficult to measure; d) precipitate formation; e) reduction could not be effected over the available potential range; f) beginning of hydrogen overvoltage (depressed); g) double wave; h) poorly developed double wave; only the approximate mean value of the half-wave potentials of both waves is given. The half-wave potentials were measured relative to the saturated calomel electrode. Ionic concentration $1 \cdot 10^{-3}$ M.

Nitrogen was used to purge oxygen from the solution before taking polarograms. It follows from the table that copper and thallium will interfere with the polarographic determination of manganese, since these elements are polarized in a potential region close to the half-wave depolarization potential of manganese; platinum and gold will also interfere since their waves precede the manganese wave.

Interference may also be shown by antimony, lead, and silver since they form precipitates in this medium, and the trivalent manganese in the form of its complex may be partially adsorbed by these precipitates. Elements which form complexes with sodium sulfosalicylate may also interfere since they depress the concentration of the sulfosalicylate in the supporting electrolyte. Accordingly in order to carry out an analysis the method of standard additions must be used.

The complex of divalent manganese with sulfosalicylic acid has been studied by Japanese research workers [7]. They used hydroxylamine hydrochloride for preventing the complex from being oxidized. The wave of the trivalent manganese complex studied in the work described in the present article is more suitable for analytical purposes because of the positive value of the half-wave potential.

Determination of manganese in siderites. A 0.2 g finely ground sample is dissolved in approximately 15 ml hydrofluoric acid and two drops of concentrated sulfuric acid contained in a platinum crucible; the mixture is heated to the appearance of white fumes. The residue in the crucible is dissolved in hot water and the solution quantitatively transferred to a 100 ml standard flask. Twelve g of sodium sulfosalicylate is added, and sodium hydroxide solution is added dropwise until an orange color appears. Sodium hydroxide is then added in sufficient amount to ensure that its final concentration in the solution in the standard flask is $5 \cdot 10^{-2}$ M. The volume of the solution is made up to the mark with water and the whole mixed. An aliquot of this solution is transferred to a Calousek cell, and after 3 min (after oxidation of the manganese complex by air) oxygen is purged from it by means of nitrogen; polarograms are taken starting at +0.1 v using anode-cathode polarization and a 2 v storage battery. The results are evaluated by the method of standard additions. Two different samples of siderite with contents of 2.06% and 1.92% manganese were analyzed in this way. The values found were 2.06% and 1.87% respectively.

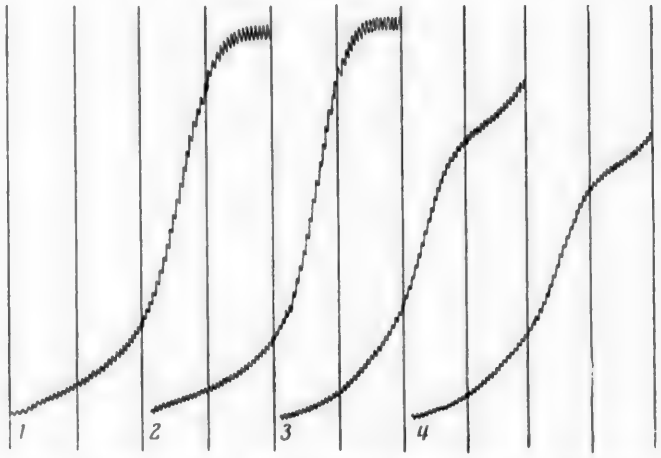

Fig. 1. Polarographic determination of manganese in siderites. Electrolyte: $5 \cdot 10^{-2}$ M NaOH and $4 \cdot 10^{-1}$ M sodium sulfosalicylate. 1) Sample; 2) ditto + 0.55 mg Mn; 3) sample; 4) ditto + + 0.55 mg Mn. Storage battery 2.0 v; S = 1/15, anode-cathode polarization (saturated calomel electrode): oxidation by air for 3 min; purging with nitrogen for 3 min.

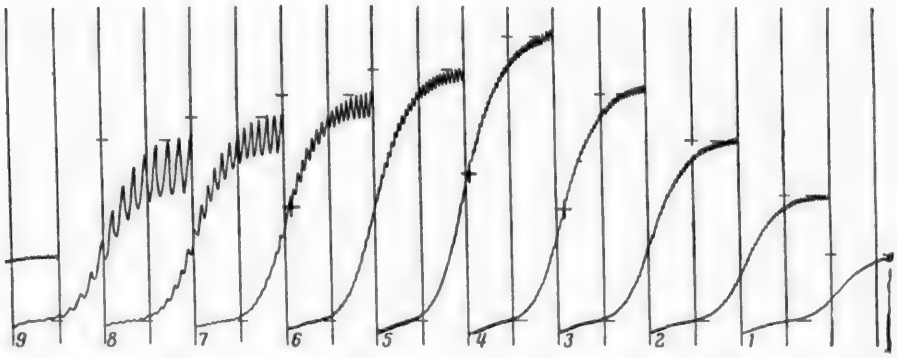

Fig. 2. Relation between wave height and manganese concentration, and between wave height and the height of the mercury reservoir. Electrolyte: $5 \cdot 10^{-2}$ M NaOH and $4 \cdot 10^{-1}$ M sodium sulfosalicylate. 1-5) $1 \cdot 10^{-3}$ M – $5 \cdot 10^{-3}$ M $MnCl_2$; 5-9) $5 \cdot 10^{-3}$ M $MnCl_2$; 5) h = 64 cm; 6) h = 49 cm; 7) h = 36 cm; 8) h = 25 cm; 9) h = 16 cm. Storage battery 2.0 v; S = 1/40; polarograms taken during anode-cathode polarization (saturated calomel electrode); oxidation by air for 3 min; purging with nitrogen for 3 min.

SUMMARY

The polarographic behavior of a number of ions in alkaline sulfosalicylate solutions has been studied, and a method has been developed for the rapid determination of manganese in mineral raw material. The reduction waves of a trivalent manganese complex were used.

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SPECTROPHOTOMETRIC DETERMINATION OF ULTRA-SMALL AMOUNTS OF NICKEL IN INDIUM

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 596-598, September-October, 1961
Original article submitted January 2, 1961

Earlier [1] we suggested α-furildioxime, which permits determination of $5 \cdot 10^{-8}$ g or $5 \cdot 10^{-6}$% of nickel in one g of indium or aluminum, for determining nickel in high purity metals. In order to determine smaller amounts of nickel without increasing the weight of metal sample, it is obvious that one must use a reagent which gives a compound with a higher molar absorption coefficient with nickel.

TABLE 1. Molar Extinction Coefficients of Compounds of Nickel with Dioximes

Reagent	λ_{max}	ϵ max [2]	ϵ^*
α-Benzyldioxim-ate	273	$4{,}03 \cdot 10^4$	$5{,}0 \cdot 10^4$ ($\lambda^* = 275$ mμ)
	361	$9{,}89 \cdot 10^3$	$1{,}0 \cdot 10^4$
	406	$1{,}09 \cdot 10^4$	$1{,}2 \cdot 10^4$
A-Furildioximate	293	$3{,}90 \cdot 10^4$	$5{,}0 \cdot 10^4$*
	384	$1{,}04 \cdot 10^4$	$1{,}0 \cdot 10^4$
	435	$1{,}52 \cdot 10^4$	$1{,}9 \cdot 10^4$

*ϵ-values were obtained by measuring the absorption of chloroform solutions of the nickel dioximates separated in the solid form.

As the results in Table 1 show, nickel dioximates have three absorption bands. Nickel α-benzyldioximate and nickel α-furildioximate absorb strongly in the ultraviolet. The reagents themselves, however, which are always taken in excess for the determination of nickel and are readily soluble in the extractants used, absorb in this spectral region.

We decided on α-benzyldioxime, since its compound with nickel is stable to the action of alkali, and, in contrast to the compound of nickel with α-furildioxime and the free reagent, can be removed from the extractant layer with a solution of sodium hydroxide (Fig. 1), so that measurements can be made at $\lambda = 273$ mμ ($\epsilon = 50{,}000$).

EXPERIMENTAL

Reagents and apparatus. All the reagents and distilled water used were carefully purified both from possible traces of nickel and from materials which exhibit characteristic absorption at 275 mμ and which can be extracted by chloroform.

Nitric acid was purified by distillation in quartz apparatus. Commercial chloroform was purified by Weisberger's method [3].

Ethanol was distilled over solid sodium hydroxide; α-benzyldioxime was twice recrystallized from dioxane. All reagents were controlled for freedom from nickel by a spectrophotometric method.

The optical density of solutions was measured on a SF-4 spectrophotometer fitted with a hydrogen lamp, cylindrical teflon cells with quartz windows and having a capacity of 2.5 ml and a path length of 100 mm being used.

The vessles used were washed with distilled nitric acid and twice distilled water, since on using sodium carbonate and a chromic mixture for washing them, contamination was introduced which distorted the experimental results. Vessels which had not been previously used, as a rule, gave low and nonreproducible results.

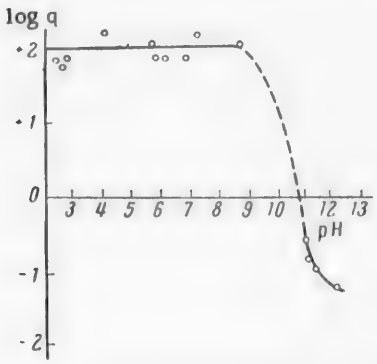

Fig. 1. The relation between the partition coefficient of α-benzyldioxime in the system H_2–$CHCl_3$ and the pH of the aqueous solution.

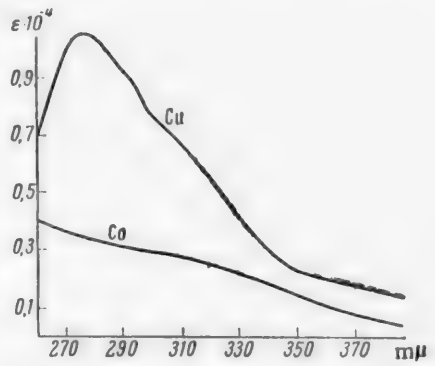

Fig. 2. Absorption spectra of metal α-benzyldioximates.

TABLE 2. Determination of Nickel in Indium (on a 1 g sample)

Nickel introduced μg	%	Found, μg	Error, %
0,010	$1 \cdot 10^{-6}$	0,010	0
0,010	$1 \cdot 10^{-6}$	0,010	0
0,020	$2 \cdot 10^{-6}$	0,022	+10
0,020	$2 \cdot 10^{-6}$	0,020	0
0,005	$5 \cdot 10^{-7}$	0,002	—60
0,005	$5 \cdot 10^{-7}$	0,003	—40
0,005	$5 \cdot 10^{-7}$	0,004	—20
0,005	$5 \cdot 10^{-7}$	0,005	0
0,005	$5 \cdot 10^{-7}$	0,0045	—10
0,005	$5 \cdot 10^{-7}$	0,006	+20

Mean arithmetic error ±16%. Mean error of individual determinations ± 25%

Conditions for determining nickel in solutions of its pure salts. Ultra-small amounts of nickel α-benzyldioximate (about 0.01 μg) are completely extracted at pH 8.0-11.3; larger amounts of nickel are extracted starting at a pH of 6.0 [4]. Completeness of extraction also depends on the ethanol concentration of the aqueous solution. The optical density is constant at ethanol concentrations not less than 20%. Variations in the ratio of the volumes of the aqueous and organic phase (from 2 to 8) do not affect the experimental results. There was very little difference between the results obtained when one and two extractions were used; accordingly, we always carried out only one extraction.

The optical density was measured relative to a solution obtained by extracting all the materials participating in the reaction (apart from nickel) with chloroform. Excess of reagent which is also extracted by chloroform and absorbs light at 275 mμ, was washed out with a sodium hyoxide solution.

Solutions of nickel α-benzyldioximate in chloroform conform to Beer's law over the concentration range 0.005 to 5 μg in 5 ml. The calibration line passes through the origin.

Cobalt and copper readily form extractable α-benzyldioximates which absorb light at 275 mμ (Fig. 2). It was established that on washing a chloroform solution of nickel, copper, and cobalt α-benzyldioximates with sodium hydroxide solution, the copper complex is completely destroyed, while three quarters of the cobalt complex is destroyed. In the case of commensurable amounts of Co and Ni, as is the case in high purity metals, the amount of cobalt which remains does not affect the experimental results.

Determination of nickel in indium metal. Under the conditions used for determining nickel, indium forms a hydroxide. Accordingly, citric and tartartic acids are added to the solution; these acids do not affect completeness of nickel extraction. One g of indium metal is dissolved in 10 ml of concentrated nitric acid contained in a quartz basin, and the solution evaporated almost to dryness. The solid residue is transferred to a separating funnel by means of 20 ml of a 20α citric acid solution and 5-10 ml of 20% potassium sodium tartrate.* Sodium hydroxide solution is then added until the pH is 8-11 according to indicator paper. Two ml of a 0.02% ethanol solution of α-benzyldioxime is then added, followed by ethanol until its concentration is not less than 20%. The contents of the funnel

*The use of tartrates alone or citrates alone invariably led to the formation of an amorphous precipitate at the pH used for extraction.

are shaken for 10-15 sec, and then extracted for 2 min with 5 ml of chloroform using a mechanical shaker. The aqueous layer is removed with a pipet. The chloroform solution is washed with two 5 ml portions of 1 N sodium hydroxide, each washing being carried out for 2 min. The optical density of the chloroform extract is finally measured at 275 mμ.

The indium sample at our disposal contained $2.8 \cdot 10^{-5}$ % nickel; this excluded the possibility of determining about 10^{-7} % nickel in it by the method of additions. Accordingly, the indium solution was purified from nickel by means of α-benzyldioxime, and then various amounts of nickel were added to the indium solution.

Results of the determination of nickel in indium are given in Table 2.

SUMMARY

Nickel can be determined with α-benzyldioxime by measuring the optical density of the compound formed in the maximum absorption region of the compound (275 mμ), after removal of excess reagent by washing the extract with alkali.

Conditions have been established for the spectrophotometric determination of ultra-small amounts (down to 0.005 μg) of nickel by means of α-benzyldioxime in solutions of its pure salts and in the presence of cobalt and copper.

A method has been developed for the determination of traces of nickel in indium metal down to a level of $5 \cdot 10^{-7}$ %; the reproducibility of the method is ±25%.

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A KINETIC METHOD FOR THE DETERMINATION OF MICROAMOUNTS OF COBALT IN SOLUTION

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 599-605,
September-October, 1961
Original article submitted November 8, 1960

Small amounts of cobalt are most often determined photometrically using nitroso-R-salt; this method permits determination of cobalt at concentrations of 1-15 μg/ml [1]. For detection of cobalt at lower concentrations several kinetic methods have been suggested which are based on the catalytic effect of cobalt on the oxidation of various reducing agents by peroxides, and, in particular, of alizarin in alkaline media [2-5]. These methods are characterized by high sensitivity, and, as Bognar [4] has shown, permit detection of 0.000001 mg cobalt in 5 ml of solution. No method has, however, hitherto been developed for the quantitative determination of cobalt by kinetic methods. The work described here is an attempt to fill this gap.

EXPERIMENTAL

When alizarin is oxidized by hydrogen peroxide the colored material disappears, and, accordingly, the optical density of the solution changes as the reaction proceeds. At room temperature and in the absence of a catalyst, this reaction proceeds very slowly.

The reaction rate was studied on a FEK-N-54 photoelectric microcolorimeternephelometer using a cell with a path length of 3 cm and a No. 3 filter (effective wavelength 453 mμ), since solutions of alizarin in a borate buffer exhibit maximum absorption at 440-460 mμ. The solutions in the cell were thermostated at 25 ± 0.1 by continuous circulation of water from a thermostat through a special housing surrounding the cell.

Solutions of hydrogen peroxide and cobalt chloride, and the buffer solutions were prepared from the chemically pure preparations. Hydrogen peroxide concentration was determined iodometrically. Since there are no methods for the determination of low concentrations of cobalt, working solutions of cobalt were prepared by accurate dilution of the original stock solution of 0.1 M $CoCl_2$, the cobalt content of which was determined electrolytically.

The alizarin solution $C_{14}H_8O_4$ (1,2-dihydroxyanthraquinone) was prepared by dissolving 0.250 g of the recrystallized material [6] in 10 ml of 0.08 N NaOH, and subsequently diluting the volume to the mark with water in a 250 ml standard flask. The concentration of one of the alizarin solutions prepared was determined titrimetrically [6]. The concentration of the remaining solutions was controlled by means of their optical density.

Borate and veronal buffer solutions were prepared according to [7]. Twice distilled water was used for preparing all the working solutions.

Reaction mixtures were prepared in a 50 ml standard flask; alizarin solution, buffer solution, water for preliminary dilution, and hydrogen peroxide were introduced successively into the flask. The reaction mixtures were thermostatted at 25 ± 0.05° for 10-15 min. Catalyst solution was then added, followed by water to bring the volume up to the mark. A stopwatch was started off when the catalyst was added. The solution was carefully mixed and transferred to the thermostatted cell. Starting from the second minute after addition of the catalyst, the optical density of the solution was measured every minute for 10 min.

The final concentrations of the solutions were as follows: alizarin, $3.3 \cdot 10^{-5}$ M (D = 0.440 at 453 mμ in a 3 cm cell); hydrogen peroxide, $3.5 \cdot 10^{-2}$ M; cobalt chloride, $1.0 \cdot 10^{-8}$ to $11.2 \cdot 10^{-8}$ M; the pH of the solution was adjusted by means of borate or veronal buffers.

After treatment of the kinetic results obtained, the cobalt concentration of the solution was determined by the method described below. In order to check on the accuracy of the results obtained, experiments were carried out

with a cobalt chloride solution labelled with Co^{60}. The concentration of the original cobalt chloride solution labelled with Co^{60} ($8.0 \cdot 10^{-5}$ M) was determined photometrically with nitroso-R-salt and the solution diluted accurately 100 times. Subsequently, in order to determine the cobalt content, the rate of the catalytic oxidation of alizarin at $CoCl_2$ concentrations ranging from $1.6 \cdot 10^{-8}$ to $11.2 \cdot 10^{-8}$ M was established, and the radioactivity of these same solutions measured on a 20 ml aliquot using a B-2 setup. The effect of foreign ions on the accuracy of cobalt determination was established. The effect of complex cobalt compounds on the rate of alizarin oxidation was also examined; these compounds included cobalt ethylenediammine, hexammine, and pentamminechloride. The experimental procedure was the same as that described above. Only the order in which the reagents were added was altered: hydrogen peroxide was added to the solution last. The stopwatch was started on adding the oxidizing agent.

DISCUSSION OF RESULTS

The rate of the catalytic oxidation of alizarin by hydrogen peroxide conforms to the equation*

$$\frac{dx}{dt} = \varkappa (a - x)\, bc, \tag{1}$$

where κ is the catalytic coefficient (the velocity constant of the catalytic reaction); $(\alpha - x)$, $\underline{x}$, $\underline{b}$, $\underline{c}$ are the current (at a given time) concentrations of alizarin, its oxidized form, cobalt chloride, and hydrogen peroxide respectively.

The current concentrations of H_2O_2 and $CoCl_2$ are almost equal to the initial concentrations, since a large excess of hydrogen peroxide is taken with respect to alizarin, while the concentration of the cobalt ion, as a catalyst, remains constant.

The initial and current concentration of alizarin are related to the optical density of the solutions in accordance with Beer's law:

$$D_0 = \varepsilon l a, \tag{2}$$

$$D = \varepsilon l (a - x), \tag{2a}$$

where D_0 is the optical density of the solution at the start; D is the optical density of the solution at a given moment; ϵ is the molar extinction coefficient; l is the path length.

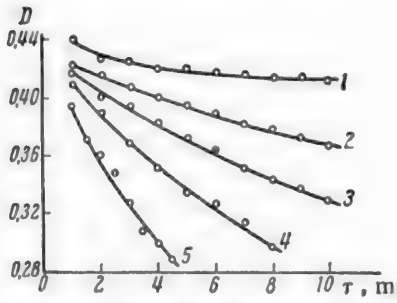

Fig. 1. Change of optical density with time during oxidation of alizarin at various $CoCl_2$ concentrations in the reaction mixture (M). 1) 0; 2) $1.3 \cdot 10^{-8}$; 3) $2.5 \cdot 10^{-8}$; 4) $5.0 \cdot 10^{-8}$; 5) $10.5 \cdot 10^{-8}$.

The change in optical density of an alizarin solution following upon its oxidation by hydrogen peroxide is shown in Fig. 1. Each curve characterizes the rate of reaction at a given cobalt ion concentration in solution. In order to get a linear relationship, it was found convenient during determination of cobalt by the kinetic method to integrate equation (1). After substituting the constants we get:

$$\lg \frac{a}{a - x} = \varkappa_1 bct. \tag{3}$$

Instead of the ratio of the initial alizarin concentration to its current concentration, the ratio of the optical densities corresponding to this ratio was substituted [equations (2) and (2a)], from this it was found that:

$$\lg D = -\varkappa_1 bct + \lg D_0. \tag{4}$$

The experimental results confirm the validity of this equation: the change in optical density with time when plotted in semilogarithmic coordinates is actually linear (Fig. 2). The slopes of these lines to the abscissa are proportional to the concentration of cobalt ions (b) at a constant H_2O_2 concentration (c):

$$\operatorname{tg} \alpha = \varkappa_1 bc. \tag{5}$$

In accordance with these equations, for determination of unknown concentrations of cobalt in solution, curves were constructed within the coordinates: cobalt concentration – tangent α (Fig. 3). When this is done all the experimental

* The rate of the noncatalytic reaction is relatively low and can be disregarded.

points lie on a straight line. There is also a linear relation between tangent α and hydrogen peroxide concentration for a constant cobalt concentration [equation (5)]. This relation breaks down, however, at high H_2O_2 concentrations (higher than 0.02 M), as is evident from Fig. 4. Such a relation between tangent α and hydrogen peroxide concentration can be explained by the formation of a peroxide complex of cobalt according to the following scheme:

$$CoOH^+ + H_2O_2 \rightleftarrows \left[Co\begin{matrix}OH\\O_2H_2\end{matrix}\right]^+, \qquad (I)$$

the stability constant β of which is defined as

$$\beta = \frac{[Co(OH)(O_2H_2)^+]}{[CoOH^+][H_2O_2]}. \qquad (6)$$

The concentrations of the complex compound, hydrogen peroxide, and total cobalt concentration are denoted respectively by C, c, and b. It follows from equation (6) that:

$$C_k = \frac{\beta bc}{1 + \beta c}. \qquad (7)$$

Since the hydrogen peroxide concentration C is low, the value of αc is also low, and it can be disregarded, since the concentration of the complex compound of cobalt is proportional to the hydrogen peroxide concentration and the total cobalt concentration, then the reaction rate depends on H_2O_2 concentration. Under these conditions the reaction rate would be described by equation (3). On increasing the hydrogen peroxide concentration above 0.02 M, the value of αc increases and becomes appreciably greater than unity, and the denominator of the fraction in equation (7) can be replaced by βc (βc approximately equal to $\beta c + 1$). Equation (7) is simplified. This corresponds to the fact that almost all the cobalt has been converted into a complex compound:

$$C_k \approx b. \qquad (8)$$

Under these conditions there appears on the curve (Fig. 4) a horizontal section for which the kinetic equation:

$$\lg \frac{a}{a-x} = \varkappa_2 bt. \qquad (3a)$$

is valid. The slope of the straight lines $\log D_0/D - t$, in this case is equal to $\varkappa_2 b$, the accuracy does not depend on the H_2O_2 concentration. The values of the catalytic coefficients calculated from the experimental results are equal, respectively to

$$\varkappa_1 = (3{,}1 \pm 0{,}7) \cdot 10^6 \frac{\text{liters}^2}{\text{moles}^2 \cdot \text{min}} \text{ и } \varkappa_2 = (6{,}4 \pm 0{,}1) \cdot 10^5 \frac{\text{liters}}{\text{moles} \cdot \text{min}}$$

at pH = 9.24.

The relation between tangent α (for a constant H_2O_2 concentration higher than 0.02 M) and the pH of the solution is expressed by a curve which passes through a maximum (Fig. 5). This feature of the relation can be explained by the fact that alizarin and its compound with tetraborate, which dissociate like acids in three stages, obviously exhibit the highest catalytic activity in the second dissociation stage which occurs in the pH range 9.2-9.4.

The fact that alizarin interacts with tetraborate is confirmed by the absorption spectra of solutions of alizarin and of alizarin and tetraborate. In the case of alizarin solutions the absorption maximum lies at 520 mμ, while in the presence of $Na_2B_4O_7$ it shifts to 440-460 mμ.

A comparison of the radioactivity of solutions labelled with Co^{60} with their catalytic activity is made in Fig. 6. The linear relation between tangent α and the radioactivity, which is proportional to the cobalt concentration, shows that the two completely independent methods of determining cobalt give the same results.

Results for the determination of cobalt in pure solutions by the kinetic method are given in Table 1.

The effect of various impurities on the accuracy of cobalt determination was established. Examination of Table 2 shows that the presence of K^+, NH_4^+, VO_3^-, I^-, F^-, SO_4^{2-}, HO_2^-, CH_3COO^-, SCN^- ions at concentrations which are 10^6 times that of the cobalt, does not essentially affect the oxidation rate. In the presence of the heavy metal ions Ba^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+}, already at concentrations which are 100-1000 times the cobalt concentration, the rate of the catalytic reaction decreases approximately twice. Tartrates, citrates, and oxalates which complex cobalt show the same effect. Cobalt can, however, be determined in these cases by applying the requisite corrections. In the presence of Cd^{2+}, Ni^{2+}, Zn^{2+}, and sodium ethylenediaminetetracetate, the oxidation reaction hardly proceeds at all and determination of cobalt is impossible.

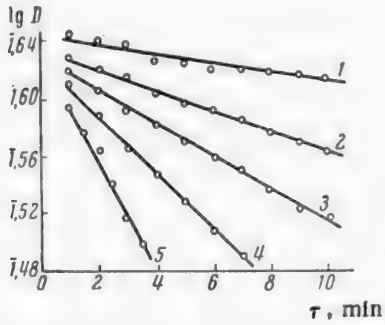

Fig. 2. Change of optical density with time, in semilogarithmic coordinates, during oxidation of alizarin at various $CoCl_2$ concentrations in the reaction mixture (M): 1) 0; 2) $1.3 \cdot 10^{-8}$; 3) $2.5 \cdot 10^{-8}$; 4) $5.0 \cdot 10^{-8}$; 5) $10.5 \cdot 10^{-8}$.

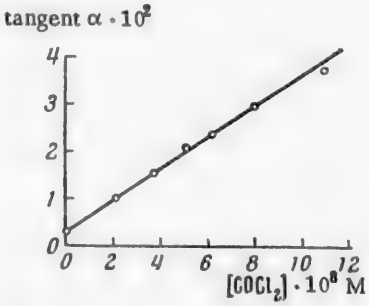

Fig. 3. The relation between the value of tangent α and cobalt concentration $[H_2O_2] = 5.2 \cdot 10^{-2}$ M; pH = 9.24; t = 25°.

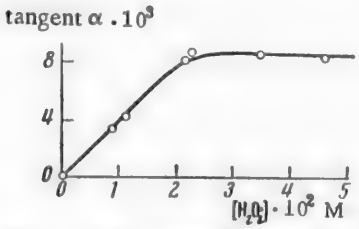

Fig. 4. The relation between the value of tangent α and hydrogen peroxide concentration $[H_2O_2] = 4.75 \cdot 10^{-8}$ M; pH = = 9.24; t = 25°.

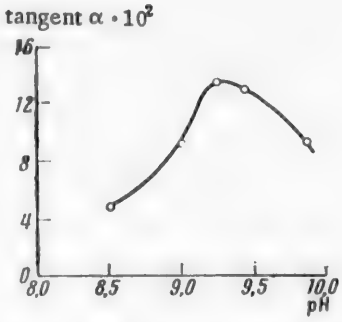

Fig. 5. The relation between the value of tangent α and pH of the solution. $H_2O_2] = 0.8 \cdot 10^{-2}$ M; $[CoCl_2] = 3.1 \cdot 10^{-6}$ M; t = 25°.

The following oxidation mechanism can be postulated to explain the catalytic action of divalent cobalt. The complex compound formed according to equation (I) can breakdown with formation of the hydroxyl radical OH and trivalent cobalt according to the scheme:

$$\left[Co\begin{matrix}OH\\O_2H_2\end{matrix}\right]^+ \rightleftharpoons Co(OH)_2^+ + \cdot OH. \qquad (II)$$

The catalyst is regenerated as a result of the reduction of Co^{III} by the hydrogen peroxide aniona:

$$Co(OH)_2^+ + O_2H^- \rightleftharpoons CoOH^+ + O_2H + OH^-. \qquad (III)$$

The perhydroxy radical $\cdot O_2H$, just like the $\cdot OH$ radical can oxidize alizarin. The products formed by the oxidation of alizarin with hydrogen peroxide in an alkaline medium could be: β [2-carboxy-1,4-diketonaphthyl-3] acrylic acid ($C_{14}H_9O_6$) and β [2-carboxy-1,4-diketonaphthyl-3] dihydroxyacrylic acid ($C_{14}H_{11}O_8$).

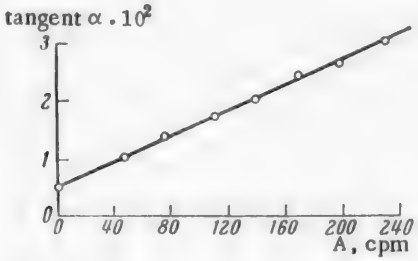

Fig. 6. Comparison of the radioactivity of $CoCl_2$ solutions labelled with Co^{60}, with their catalytic activity. $[H_2O_2]$ = $= 3.8 \cdot 10^{-2}$ M; pH = 9.24; t = 25°.

TABLE 1. Determination of Cobalt in Solution by the Kinetic Method

Cobalt taken, M × × 10^8	No. of expts.	Cobalt found by means of the calibration curve, M × 10^8	Mean deviation × 10^8
2.9	3	3.2	±0.2
3.9	3	4.2	±0.4
4.8	3	4.7	±0.4
5.8	3	6.2	±0.4
7.2	3	7.5	±0.4

Stable complex compounds of Co^{III} do not possess any appreciable catalytic activity. Thus cobalt ethylenediammine $Co(en)_3$ (instability constant $2.04 \cdot 10^{-49}$ [8]) does not affect the rate of alizarin oxidation, while the catalytic activity of the cobaltammines $Co(NH_3)_6^{3+}$ (instability constant $3.1 \cdot 10^{-33}$ [8]) and $Co(NH_3)_5^{2+}$ (instability constant $1.85 \cdot 10^{-6}$ [7]) is ten thousand times weaker than the activity of the free cobalt cation. Addition of ammonia to a solution containing a cobaltammine sharply depresses the catalytic activity.

TABLE 2. Effect of Foreign Ions on the Results of Cobalt Determination in Solution by the Kinetic Method

Foreign ion	Ratio of foreign ion concentration to cobalt concentration	Slope of the line to the abscissa · 10^{+2}	Foreign ion	Ratio of foreign ion concentration to cobalt concentration	Slope of the line to the abscissa · 10^{+2}
—	—	7,2	MoO_4^{2-}	$6{,}0 \cdot 10^4$	1,1
K^+	$1{,}0 \cdot 10^5$	7,2	WO_4^{2-}	$1{,}0 \cdot 10^4$	2,9
NH_4^+	$1{,}0 \cdot 10^5$	7,2	VO_3^-	$3{,}0 \cdot 10^3$	7,2
Ba^{2+}	$7{,}0 \cdot 10^3$	3,8	I^-	$2{,}0 \cdot 10^5$	7,2
Ca^{2+}	$4{,}0 \cdot 10^3$	3,3	F^-	$2{,}0 \cdot 10^5$	7,2
Mg^{2+}	$4{,}0 \cdot 10^3$	4,6	SO_4^{2-}	$2{,}0 \cdot 10^5$	7,2
Sr^{2+}	$2{,}0 \cdot 10^3$	4,6	SCN^-	$2{,}0 \cdot 10^5$	7,2
Cu^{2+}	$8{,}0 \cdot 10^3$	4,0	CH_3COO^-	$2{,}0 \cdot 10^5$	7,2
Cd^{2+}	$2{,}0 \cdot 10^3$	0	NO_2^-	$2{,}3 \cdot 10^5$	7,2
Ni^{2+}	$2{,}0 \cdot 10^3$	0	PO_4^{3-}	$2{,}0 \cdot 10^5$	6,3
Zn^{2+}	$1{,}5 \cdot 10^2$	0,2	Tartrate	$4{,}0 \cdot 10^4$	4,0
Pb^{2+}	$1{,}6 \cdot 10^2$	5,6	Citrate	$1{,}8 \cdot 10^4$	3,8
Mn^{2+}	$1{,}0 \cdot 10^3$	6,0	Oxalate	$1{,}9 \cdot 10^3$	2,1
Sn^{2+}	$5{,}3 \cdot 10^3$	7,0	Sodium ethylenediaminetetracetate	$1 \cdot 10^3$	0
Al^{3+}	$1{,}0 \cdot 10^3$	4,1			
Fe^{3+}	$1{,}0 \cdot 10^3$	3,1			
Gr^{3+}	$2{,}0 \cdot 10^2$	3,6			

SUMMARY

A study has been made of the catalytic oxidation of alizarin by hydrogen peroxide in an alkaline medium in the presence of cobalt salts. It has been established that the rate of this reaction is proportional to the cobalt and alizarin concentrations. A kinetic equation has been derived and a mechanism is postulated for the reaction studied.

Using the reaction studied a method has been developed for the quantitative determination of cobalt at concentrations of the order of 10^{-8} M.

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DETERMINATION OF PLATINUM IN THE PRESENCE OF PALLADIUM BY POTENTIOMETRIC TITRATION WITH A CUPROUS CHLORIDE SOLUTION

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 606-610, September-October, 1961
Original article submitted January 5, 1961

Chloroplatinates interact with Cu_2Cl_2 according to the equation: $PtCl^{2-} + 2Cu^{I} \rightleftharpoons PtCl_4^{2-} + 2Cu^{2+} + 2Cl^{-}$, Muller [1] was the first to make use of this reaction for the determination of platinum by potentiometric titration. Recently, research has been directed [2, 3] towards establishing the requisite experimental conditions more accurately, and at simplifying the technique of determining quadrivalent platinum quantitatively by titration with Cu_2Cl_2 solution.

The authors of these papers have observed that the nature of the titration changes and the accuracy with which platinum is determined decreases as the hydrochloric acid content of the solution increases. It was established that titration can be carried out both at room temperature, and on heating the solution to 50-70°, and that chlororhodiates do not interfere with platinum determination. Nevertheless, when chlororhodiates are present in solution, quadrivalent iridium is reduced and is titrated together with quadrivalent platinum with a common potential jump. Under certain conditions of temperature, acidity of solution, and ratio of chloroiridate and chloroplatinate concentrations in solution, two potential jumps are observed during titration: one corresponds to completion of reduction of Ir^{IV} to Ir^{III}, while the other corresponds to completion of reduction of Pt^{IV} to Pt^{III}.

Grinberg and Maksimyuk [3] have also shown that it is possible to determine quadrivalent platinum by titrating with a solution of Cu_2Cl_2 in the presence of the complex chlorides of divalent palladium. Published results relate to the determination of platinum in hydrochloric acid solutions of chloroplatinates, containing palladium in amounts approximately equal to or somewhat less than the platinum content.

When we tried to use potentiometric titration for the quantitative determination of platinum in solutions containing preponderant amounts of palladium, we came up against some difficulties which made it necessary to carry out an additional study of the effect of palladium on the character of the titration, and on the accuracy of platinum determination.

Reagents and apparatus. Our work was carried out on a synthetic mixtures prepared from solutions of chloroplatinic acid and sodium chloropalladiate of known concentration (about 1 mg/ml), containing hydrochloric acid (1-2%) and sodium chloride (up to 2%).

Cuprous chloride was prepared by the method recommended by Gregor [4] or the commercial material (analytical grade) was used. When the reagent was partially oxidized it was washed with a small amount of hydrochloric acid and water for removing $CuCl_2$.

Cu_2Cl_2 solution (0.01-0.03 N) in hydrochloric acid was prepared according to the method given in Grinberg's paper, and it was stored in a dark colored flask in a carbon dioxide atmosphere [2, 3]. The Cu_2Cl_2 solution was standardized against a standard solution of chloroplatinic acid. Potentiometric titration was carried out on a compensation setup with a type PPTV potentiometer and a galvanometer which permits the emf to be determined with an accuracy of 1 mv. A platinum wire or a gold disc was used as the indicator electrode, while a saturated calomel electrode was used as the reference electrode.

EXPERIMENTAL

The original solution containing platinum, or platinum and palladium, in the form of their complex chlorides, was evaporated carefully on a water bath to the moist salt state (sodium chloride should be present to prevent hydrolysis of palladium salts). The dry residue was dissolved in hydrochloric or sulfuric acid of a known concentration and the solution transferred to titration vessel. The volume of solution being titrated was 50 ml. CO_2 was passed through the liquid for 5-10 min before starting a titration in order to remove the air. Titration was carried out at room temperature while the solution was continuously stirred and the system was carefully isolated from atmospheric oxygen by means of CO_2.

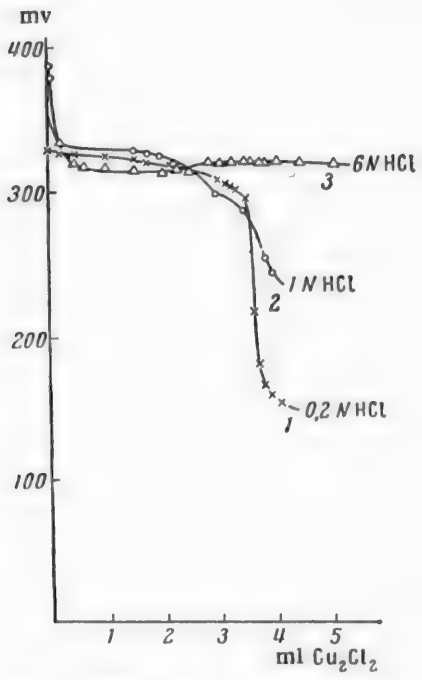

Fig. 1. Effect of hydrochloric acid concentration on titration of chloroplatinate with Cu_2Cl_2. 5.16 mg Pt taken. Theoretical amount of Cu_2Cl_2 that should be used 3.61 ml. Amount of Cu_2Cl_2 used for titration, ml: 1) 3.60; 2) 3.70; 3) not titrated. Pt found by titration, mg: 1) 5.15; 2) 5.29; 3) not determined.

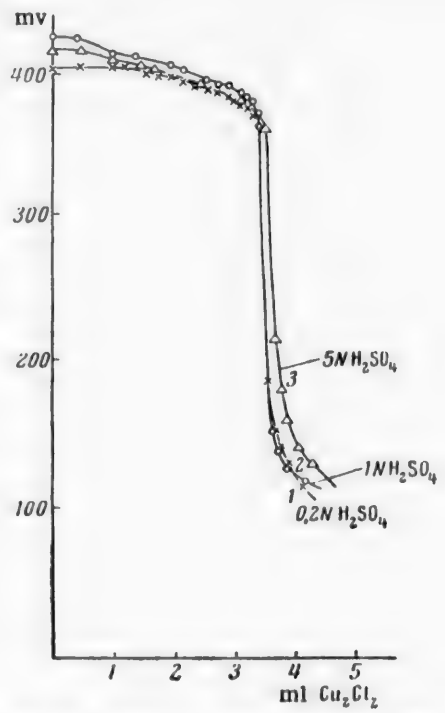

Fig. 2. Effect of sulfuric acid concentration on titration of chloroplatinate with Cu_2Cl_2 solution. 5.16 mg Pt taken. Theoretical amount of Cu_2Cl_2 that should be used, 3.61 ml. Amount of Cu_2cl_2 used for titration, ml: 1) 3.60; 2) 3.60; 3) 3.70. Pt found by titration, mg: 1) 5.15; 2) 5.15; 3) 5.20.

The experiments which we carried out confirmed that in solutions containing a smaller amount of palladium than platinum, the complex chlorides of quadrivalent platinum are titrated with a clearly defined potential jump at the equivalence point, while platinum is determined with the same accuracy as in pure solutions.

As the concentration of palladium increased with respect to that of platinum, the character of the titration curve for quadrivalent platinum changes in that the value of the potential jump at the equivalence point decreases, while in some instances no jump is observed at all.

In such cases, after reduction of quadrivalent platinum to its divalent state, deposition of metallic palladium (particularly in solutions < 0.1 N HCl) is sometimes observed; this may be a qualitative indication of the completeness of reduction of quadrivalent platinum. It was observed that when the palladium concentration exceeds the platinum concentration by an insignificant amount, a certain increase in the acidity of the solution being titrated enables reduction of palladium to its metallic form to be held back, and a potential jump to be observed during titration of

platinum. Nevertheless, satisfactory results are only obtained for determination of platinum in solutions whose acidity does not exceed 1.0 N HCl (Fig. 1).

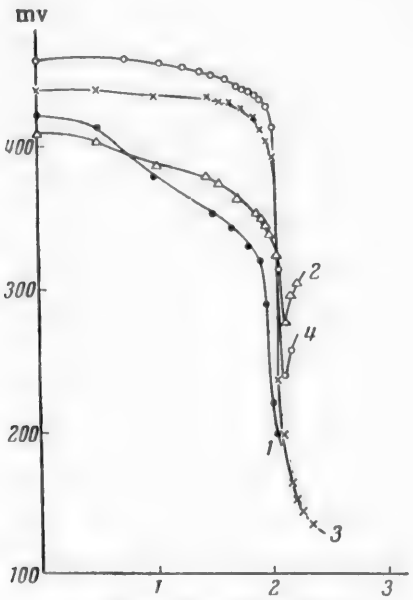

Fig. 3. Change in the value of the potential jump at the equivalence point as a function of the relative contents of Pt and Pd in solution, and of the material of the indicator electrode. 1) 3.10 mg Pt and 3.05 mg Pd taken. 1.99 equiv. Cu_2Cl_2 used. 3.08 mg Pt determined; 2) 3.10 mg Pt and 6.10 mg Pd taken. 2.04 equiv. Cu_2Cl_2 used. 3.16 mg Pt found; 3) 3.10 mg Pt and 3.05 mg Pd taken. 2.05 equiv. Cu_2Cl_2 used. 3.18 mg Pt found; 4) 3.10 mg Pt and 6.10 mg Pd taken. 2.05 equiv. Cu_2Cl_2 used. 3.18 mg Pt found.

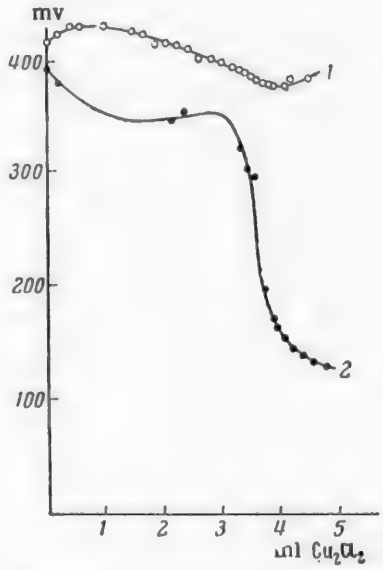

Fig. 4. The change in the character of the titration of chloroplatinate with Cu_2Cl_2 solution in the presence of palladium after addition of KI. 1) 5.16 mg Pt and 30.5 mg Pd taken. 1.0 N H_2SO_4 No KI present. 5.36 mg Pt found; 2) 5.16 mg Pt and 30.5 mg Pd taken. 1.0 N H_2SO_4. 5.9 ml of 0.1 N KI added. 5.22 mg found.

However, when the solution being titrated was acidified, not with hydrochloric acid, but with sulfuric acid, the character of the titration curve and the value of the potential jump hardly changed at all on changing the sulfuric acid concentration over a fairly wide range (Fig. 2). Neither did the presence of sodium chloride (up to 2%) affect the character and the results of the titration of chloroplatinates with Cu_2Cl_2 solution.

Table 1 contains results for the determination of platinum in pure solutions of chloroplatinates, and in solutions containing chloropalladiates as well, when the solutions were acidified with sulfuric acid.

Thus experiments have shown that in sulfuric acid solutions, quadrivalent platinum is titrated with a clearly defined potential jump at the equivalence point, and is determined with satisfactory accuracy.

Nevertheless, even in this case there is observed a change in the value of the potential jump at the equivalence point as a function of the platinum and palladium contents in the solution (Fig. 3, curves 1 and 2).

It was observed that the value of the potential jump at the equivalence point depends to some extent on the material of the indicator electrode. Thus in the case of a gold electrode the potential jump is slightly higher (Fig. 3, curves 3 and 4) than when a platinum wire is used as the indicator electrode (Fig. 3, curves 1 and 2). But in this case, as in the other, the potential jump decreases as the palladium content increases with respect to platinum content in the solution being titrated, while the results for platinum determination show a tendency to increase. At a

sufficiently high relative concentration of palladium in solution (e.g., Pt: Pd about 1: 6) the potential jump on the titration curve is almost unobservable (Fig. 4, curve 1).

In the case of solutions which contained considerably more palladium than platinum we succeeded in obtaining satisfactory results for pitainum by adding potassium iodide to the solution before titration. Despite the fact that chloroplatinate also reacts with potassium iodide [5, 6], as long as the solution contains palladium, precipitation of the latter as sparingly soluble PdI_2 occurs first. The palladium content of the solution is determined beforehand on a separate aliquot by titrating with KI according to a method suggested by Pshenitsyn and Ginsburg [7]. KI in the form of a 0.1 N solution is then added directly to the solution in the titration vessel in an amount which ensures precipitation of most of the palladium and leaves about 1 mg or less unprecipitated. This technique leads to a change in the ratio of the concentration of platinum to palladium such that there is more platinum than palladium, so that the platinum can be determined. It must be pointed out that excess potassium iodide should not be added, since in such cases the platinum will react with iodide ions and subsequent titration with Cu_2Cl_2 solution will not give satisfactory results.

TABLE 1. Determination of Platinum in the Presence of Palladium (0.02-0.05% NaCl. H_2SO_4 concentration from 0.2 N to 1 N. Platinum indicator electrode)

Taken		Pt found, mg	Error, mg	Taken		Pt found, mg	Error, mg
Pt, mg	Pd, mg			Pt, mg	Pd, mg		
8,4	—	8,4	0	5,4	3,0	5,3	—0,1
8,4	—	8,3	—0,1	6,5	3,0	6,6	+0,1
10,3	—	10,3	0	6,5	6,10	6,5	0
5,4	0,9	5,5	+0,1	10,3	10,4	10,3	0

TABLE 2. Determination of Platinum in the Presence of Preponderant Amounts of Palladium

Taken		Pt found, mg	Error, mg
Pt, mg	Pd, mg		
5,4	6,1	5,4	0
6,5	15,2	6,5	0
8,4	20,8	8,3	—0,1
5,4	30,5	5,5	+0,1
10,8	61,0	10,8	0

In Fig. 4 are shown titration curves of chloroplatinate in a solution containing chloropalladiate (Pt: Pt about 1: 6) to which no potassium iodide (curve 1) has been added, and after precipitation of most of the palladium with potassium iodide (curve 4).

Results of platinum determinations in the presence of palladium after precipitation of most of the latter with potassium iodide are given inTable 2. As these results show, the experimental error varies over the same limits as those observed during titration of pure solutions of chloroplatinates.

SUMMARY

It has been shown that the sulfuric acid content of solutions of chloroplatinate which are being titrated can be varied over a wide range, and that this variation in acidity does not affect the accuracy of platinum determination by titration with Cu_2Cl_2 solution.

As the palladium concentration of a solution increases with respect to platinum concentration, the potential jump on the titration curve decreases, and, in some cases, is not observed at all.

When chloroplatinates are titrated with Cu_2Cl_2 solution in the presence of palladium a greater potential jump is observed at the equivalence point when a gold electrode rather than a platinum electrode is used as indicator electrode.

On precipitating most of the palladium by adding KI directly to the titration vessel, it is possible to determine platinum in this solution, a clearly defined potential jump being obtained at the equivalence point.

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RAPID COMPLEXOMETRIC DETERMINATION OF BARIUM SULFATE IN BARYTA MINERALS

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 611-612, September-October, 1961
Original article submitted October 31, 1960

The barium sulfate content of minerals is usually determined by the very cumbrous classical gravimetric method. This article is devoted to variants of a simple, rapid complexometric method which permit rapid determination of barium sulfate in minerals. The results obtained by this method agree with the results obtained by the classical method.

Complexometric method using alkaline fusion of the mineral. The method is based on dissolving barium sulfate in excess of a standard solution of sodium ethylenediaminetetracetate (EDTA-Na) and titrating excess of the latter with barium chloride solution.

A 0.2-0.25 g aliquot of finely ground baryta mineral is weighed in a platinum crucible, it is fused with a mixture of sodium and potassium carbonates, and the crucible plus the fused melt immersed in a beaker containing 100 ml of hot water, and the whole boiled for several minutes. Concentrated hydrochloric acid is added carefully until gas ceases to be evolved; a further 20-25 ml of acid is added together with 1-2 ml of 10% sulfuric acid. This leads to quantitative precipitation of barium sulfate in the form of fine particles, while all the remaining components of the mineral dissolved, and the silica remains in a colloidal form. The precipitate is filtered off and washed with hot water, the filter plus precipitate are transferred into a conical flask, and a small amount of distilled water added, followed by 25-30 ml of 0.1 N EDTA-Na; the whole is mixed while hot until a completely transparent solution is obtained [1].

Results of the Determination of $BaSO_4$ in Baryta Minerals

Sample No.	$BaSO_4$ content of the mineral, %		
	by the classical method	by the complexometric method	
		after alkali fusion	without alkali fusion
1	58.80	59.04	59.28
	58.94	59.11	59.32
	59.11	59.23	59.37
2	40.49	40.67	40.62
		40.46	
3	30.82	31.02	31.10
4	54.10	54.11	54.27
5	64.10	64.20	64.33

After the volume is diluted to 200-250 ml, 8-10 ml of concentrated ammonia is added, followed by 2-3 drops of an indicator solution of phthalein-complexon; excess EDTA-Na solution is then titrated with 0.1 N barium chloride solution. At the equivalence point the color of the solution changes sharply from a pale-rose to a bright-violet [2, 3].

A determination takes approximately 3 hr.

* Translated from French by P. K. Agasyan.

The barium sulfate content is calculated by means of the formula:

$$\%BaSO_4 = \frac{(A-B)\cdot 0.0116713\cdot 100}{G}$$

where A is the number of ml of 0.1 N EDTA-Na used for dissolving the precipitate; B is the number of ml of 0.1 N barium chloride used for titrating excess EDTA-Na.

One ml of 0.1 N EDTA-Na corresponds to 0.0116713 g $BaSO_4$.

Complexometric method without alkali fusion. All operations are carried out directly on the untreated mineral, the alkali fusion operation being omitted.

Two-three ml of concentrated sulfuric acid is added to 0.2-0.25 g of mineral contained in a 100 ml beaker and the whole stirred with a glass rod. The mixture is heated for 2-3 min while stirring, until white fumes appear. The beaker is then cooled and 2-3 ml of distilled water carefully added, followed by 50-60 ml of hydrochloric acid (1:2) the mixture is boiled for 15 min and then allowed to stand for insoluble materials to settle out.

The insoluble residue is separated by decantation. The residue contains fine particles of barium sulfate, insoluble silica, and small amounts of calcium. The residue in the beaker is covered with a concentrated solution of ammonium carbonate and the whole stirred with a glass rod for 15 min until the calcium sulfate has changed into the carbonate. The mixture is then filtered, and the precipitate washed, first with a small amount of ammonium carbonate, and then with a hot, dilute solution of hydrochloric acid, and hot distilled water.

The filter plus precipitate containing barium sulfate and silica are transferred to a conical flask and treated with EDTA-Na solution as indicated above. The insoluble silica remains as a suspension. The solution is diluted to 200-250 ml and excess EDTA-Na titrated in an ammoniacal medium in the presence of phthaleincomplexon.

A determination takes about the same time as the first variant.

The results obtained by these variants are compared in the table with those obtained by the classical gravimetric method.

Reagents used: 1) 0.1 N EDTA-Na. 18.61 g of EDTA-Na and 3.8-3.9 g of sodium hydroxide (pellets) are dissolved in distilled water in a one liter standard flask and the volume made up to the mark with water. The solution is standardized complexometrically against 0.1 N standard barium chloride solution.

2) 0.1% Phthaleincomplexon solution. Twenty mg of the preparation is moistened with 1-2 drops of concentrated ammonia solution, after which it is diluted with 20 ml of distilled water. The solution does not keep for longer than a week.

SUMMARY

A rapid complexometric method is proposed for the determination of the barium sulfate content of baryta minerals; it is based on dissolving $BaSO_4$ in excess EDTA-Na solution, and titrating the excess with barium chloride solution in the presence of phthaleincomplexon.

A determination takes 3 hr; the results obtained are accurate and reproducible.

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DETERMINATION OF SULFUR, CHLORINE, AND FLUORINE IN BERYLLIUM OXIDE BY A SPECTROGRAPHIC METHOD

I. A. Berezin and K. V. Aleksandrovich

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 613-616, September-October, 1961
Original article submitted September 22, 1960

Determination of small amounts of sulfur and halogens by spectrographic analysis is a very complex problem because their spectral lines, which are located in the visible and ultraviolet regions of the spectrum, and which can only be taken advantage of when special spectrographic apparatus is available, have high excitation potentials and are difficult to excite in a flame, arc, and spark. The sensitivity with which sulfur and the halogens can be determined, even in such powerful impulse sources as a condensed spark and a low voltage spark, does not exceed some hundredths of a percent [1-11]. Such sensitivity is not enough in a number of analytical problems, in particular for the determination of sulfur, chlorine, and fluorine in beryllium oxide. Methods recommended for the spectrographic analysis of beryllium oxide in which an electric arc is used [12-15] do not ensure the possibility of determining small amounts of sulfur and halogens either.

We have developed a technique involving the use of a hollow cathode which permits determination of thousandths of a percent of sulfur, chlorine, and fluorine in beryllium oxide.

McNally, Harrison, and Rowe [16] were the first to use a hollow cathode for determining sulfur and halogens; these authors, using the lines located in the infrared determined down to 1 μg sulfur, 0.2 μg chlorine, and 0.01 μg fluorine. Their method was developed further by Chaika [17] who determined ten thousandths of a percent of fluorine and thousandths of a percent of chlorine in uranium oxide and thorium oxide. Korovin and Lipis [18] have shown that a hollow cathode can be successfully used for the determination of many elements in metals having a high boil-point. The advantages of a hollow cathode over other light sources for the determination of elements which are difficult to excite is explained by the simultaneous combination of high electronic and ionic temperature, discharge stability, low diffusion of the atoms from the discharge zone, and heating of the cathode material to the temperature necessary for evaporation of test material.

A schematic diagram of the vacuum setup which we used in our work is shown in Fig. 1.

The vacuum setup consists of evacuating and circulating systems. The air is pumped out with a RVN-20 prevacuum pump and a TsVL-100 oil diffusion pump. The vacuum is measured with a LT-2 thermoelectric tube. The discharge in the hollow cathode is carried out in an atmosphere of spectrographically pure helium which is introduced into the setup by means of a capillary tap [19]. The helium pressure is measured with an oil manometer. A DRN-10 mercury diffusion pump is used for circulating the helium. The helium is continuously purified during circulation of the gas, by means of a trap containing activated charcoal cooled with liquid air. Traps containing liquid nitrogen fitted in front of the diffusion pump are used for freezing out oil and mercury vapors.

When a hollow cathode is used, a considerable amount of time is taken up in pumping out the gas discharge tube. Moreover, when the tube is dismantled frequently, this being necessary for changing the electrodes, a considerable amount of helium is lost. Accordingly, we used a specially designed tube which enabled rapid replacement of electrodes without destroying the vacuum (Fig. 2). The molybdenum glass tube has two inlets made of molybdenum wire. Six molybdenum rods with a diameter of 1.2-1.5 mm are fused into the stopper of the tube; they are arranged around the periphery on which the hollow cathodes are fitted. The ground joint of the stopper is lubricated with a liquid vacuum grease which ensures free rotation of the stopper. Electrical contact between the hollow cathodes and the current supply is established by contact of the molybdenum rods with an elastic nickel disc fastened onto the lead-in made from molybdenum wire, fitted in such a way that it does not screen the light emitted by the hollow cathodes and does not hinder adjustment of the hollow cathodes.

The shape and dimensions of the cathodes are shown in Fig. 3. The choice of cathode material is of considerable importance. Cathodes of charcoal and graphite are completely unsuitable for analysis of oxides, since reduction reactions occur in the heated electrodes with formation of large amounts of carbon oxides whose presence in the discharge strongly depresses the sensitivity with which elements which are difficult to excite can be determined. At temperatures above 1000° the iron which starts to pass from iron and steel cathodes also lowers the accuracy and sensitivity of determination. It would be desirable to make cathodes from infusible metals: molybdenum, tantalum, or tungsten. Nevertheless preparation of such electrodes is associated with difficulties in the mechanical treatment of these materials. Good results can be obtained on using electrodes made from stainless steel the inner walls of such electrodes being protected with a tube of pure molybdenum.

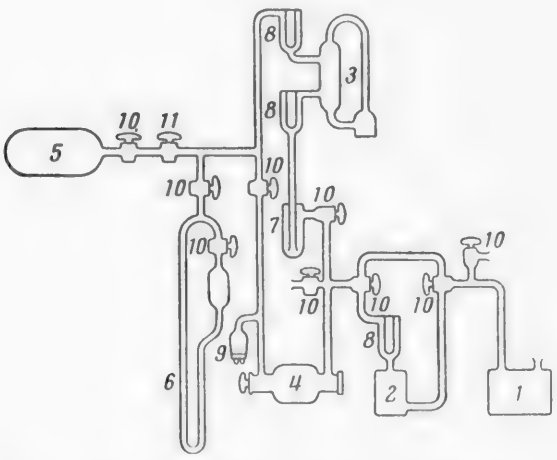

Fig. 1. Schematic diagram of the vacuum setup. 1) Prevacuum pump; 2) oil diffusion pump; 3) mercury diffusion pump; 4) tube plus hollow cathodes; 5) helium cylinder; 6) oil manometer; 7) trap with activated charcoal; 8) trap with liquid air; 9) manometer tube; 10) taps; 11) capillary tap.

Standards containing from 0.001 to 0.1% sulfur, chlorine, and fluorine are prepared from solutions of beryllium sulfate, beryllium chloride, and ammonium tetrafluoroberyllate, using pure beryllium oxide as the base. The standard samples are dried at 105-110° and are then ground up in an agate mortar.

Fifty mg samples of beryllium oxide are packed into the hollow cathodes. The discharge tube is evacuated to a pressure of $10^{-4} - 10^{-5}$ mm Hg and is then filled with helium to a pressure of 15 mm Hg. During the discharge process the helium is continuously purified by circulating it through the trap containing activated charcoal.

Spectra are photographed with an ISP-51 spectrograph fitted with a camera having $f = 270$. The slit width is 0.01 mm. The image of the hollow cathode is projected onto the slit by means of a one lens condenser.

The spectrograph casette is loaded with a composite plate such that the 4700-6000 A region is photographed on a "micro" type photographic plate, while the 6500-8000 A region is photographed on "Infra-760" type photographic plates. Before they are used the "Infra-760" plates are hypersensitized by immersing them for one minute in 5% aqueous ammonia and then drying them with a stream of air.

Two type UIP-1 rectifiers connected in series are used as the current source, the voltage of the rectified current being 1200 v. The current is regulated with a rheostat having a resistance of 6300 ohms and amounts to 300 μa. Exposure time is 2 min. At the end of this period sulfur and chlorine have "burnt out" completely; most of the fluorine also "burns out." (Table 1). The slower passage of fluorine into the discharge is explained by the fact that beryllium fluoride has a higher melting point and boiling point than beryllium sulfate and chloride.

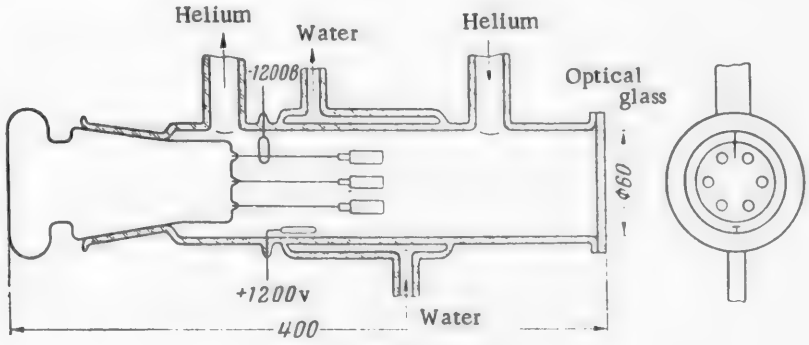

Fig. 2. Discharge tube.

The high stability of the discharge in the hollow cathode and the small background in the visible region of the spectrum enables calibration curves to be constructed for the determination of sulfur and chlorine in the coordinates (S, log C), where S is the absolute blackening of the spectral lines and C is the concentration of the element in the standards. Because of the continuous background in the infrared, the curve for determination of fluorine is constructed within the coordinates log $I_{line + background} - I_{background}/I_{background}$, log C), where $I_{line + background}$ is the intensity of the spectral line, $I_{background}$ is the background intensity, and C is the concentration (Fig. 4). In order to convert from blackening to intensity, use is made of the characteristic curve of the "Infra-760" photographic plate, constructed on the basis of the blackening marks.

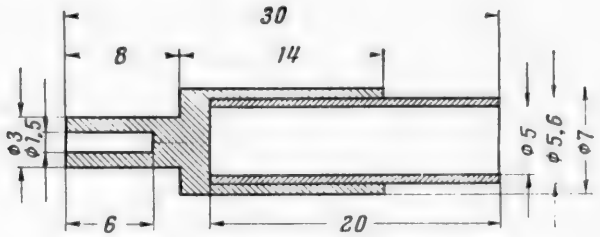

Fig. 3. Hollow cathode.

TABLE 1. "Burning Out" of Sulfur, Chlorine, and Fluorine from Beryllium Oxide in a Hollow Cathode (standard 0.01%)

Element	Spectral line, A	Difference between the blackening of the spectral line and the background, sec			Chemical compound	Notes
		0.120	120-240	240-360		
Sulfur	5453.9	0.71	–	–	$BeSO_4$	Decomposes at 550-600°
Chlorine	4794.5	0.66	–	–	$BeCl_2$	Boils at 520° (p = 760 mm Hg)
Fluorine	7037.4	0.38	0.20	–	$(NH_4)_2BeF_4$	On heating decomposes with formation of BeF_2 which melts at 800°

TABLE 2. Determination of Fluorine in Beryllium Oxide

Batch No.	Sample No.	Fluorine content, %	Mean value of the fluorine content, %	Absolute error, %	Mean absolute error, %	Mean absolute error, %
1	1	0.041	0.042	−0.001	±0.004	±9.5
	2	0.036		−0.001		
	3	0.041		−0.006		
	4	0.050		+0.008		
2	1	0.030	0.027	+0.003	±0.004	±15
	2	0.020		−0.007		
	3	0.030		+0.003		
	4	0.032		+0.005		
	5	0.024		−0.003		

The analytical lines used are: sulfur, 5453.9; chlorine, 4794.5; fluorine 7037.4. The sensitivities for the determination of the various elements are: 0.001% chlorine, 0.003% sulfur, and 0.005% fluorine.

Using this technique we have analyzed several batches of beryllium oxide. The fluorine content of two batches was determined (Table 2).

No sulfur and chlorine were found in the test samples. Accordingly, we checked on the reproducibility of the method by taking repeated photographs of standards. The mean relative error proved to be ±15-20%.

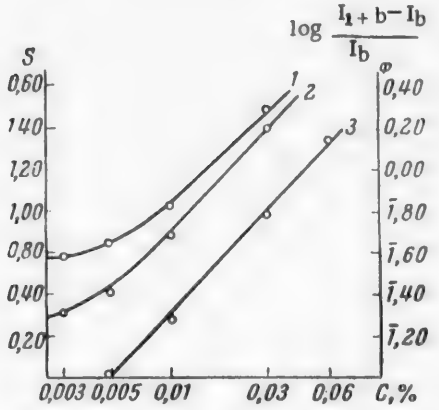

Fig. 4. Calibration curves. 1) Sulfur 5453.9; 2) chlorine 4794.5; 3) fluorine 7037.4/background.

SUMMARY

A method has been developed for the spectrographic determination of sulfur, chlorine, and fluorine in beryllium oxide by means of a hollow cathode. The method permits determination of 0.001% chlorine, 0.003% sulfur, and 0.005% fluorine in samples weighing 50 mg. The mean relative error is ± 15-20%.

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DETERMINATION OF SMALL AMOUNTS OF SULFUR IN TUNGSTEN AND MOLYBDENUM

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 617-619, September-October, 1961
Original article submitted September 27, 1960

The methods which are capable of giving the most reliable results during determination of small amounts of sulfur are those which require the minimum amounts of reagents to carry them out.

The combustion method would appear to be the most acceptable one from this viewpoint. Bruns, Braude, and Tsiklis[1] have suggested measuring the change in the concentration of the absorption solution on the basis of its electrical conductivity during carbon determination, and have extended this method to the determination of sulfur by absorbing the sulfur dioxide formed with hydrogen peroxide [2]. We have tried to determine sulfur by precipitating it in the form of barium sulfate.

It is impossible, however, to achieve a sufficiently high sensitivity by this method for the reliable determination of 0.0001% sulfur.

A considerable increase in the sensitivity with which sulfur can be determined is achieved by measuring the electrical conductivity when the sulfur dioxide is absorbed with an aqueous iodine solution. Under such conditions, for each atom of sulfur there appear in solution seven ions, four of which are hydrogen ions possessing an anomalously high mobility. Molecular iodine hardly dissociates at all into ions in water and does not increase the dissociation of water; accordingly, the electrical conductivity of the saturated solutions of iodine in water is determined mainly by the electrical conductivity of the water itself whose value is low.

The setup for sulfur determination is similar to the setup for carbon determination [1, 3, 4]. The modifications made to the setup in [4] involve the following:

a) the wash flask for absorbing sulfur dioxide was omitted; the combustion tube was connected through a tap with an absorption vessel which also acts as a measuring cell;

b) since even traces of moisture which condense on the cold parts of the apparatus almost completely absorb sulfur dioxide, the oxygen passing into the combustion tube must be dried. For this purpose a U-shaped tube containing calcium chloride was fitted between the combustion tube and the wash vessel containing alkali.

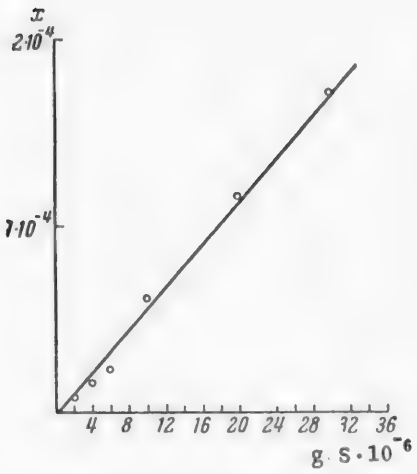
Firstly, we checked on the proportionality between the change in electrical conductivity and sulfur content. For this purpose the requisite amount of $ZnSO_4$ was calcined at a temperature of 1200°. Zinc sulfate was placed in the form of a solution in a boat; the solution was then evaporated in a drying oven. The curve shown in the diagram was obtained in this way.

The sensitivity of the method amounts to 0.2-0.3 μg sulfur. It depends mainly on the accuracy with which the electrical conductivity is measured. This same curve served further as a calibration curve for determination of sulfur in tungsten and molybdenum.

Tungsten was examined first, because fewer difficulties arise when this metal is used. Tungsten is readily oxidized and lumps of metal can be used for analysis. In addition, the tungsten trioxide formed at the combustion temperature is sparingly volatile, so that there is no need for any after charge. Before taking samples the lumps of tungsten were carefully washed with acetone and dried. Two-three g of tungsten was placed in a quartz boat calcined beforehand in an oxygen stream at a temperature somewhat higher than the combustion temperature.

Boat plus sample were then placed in the cold zone of the combustion tube; the tube was sealed and purged with an oxygen stream for 30 min. During this period the measuring cell was washed several times with a saturated

solution of iodine in water. The iodine solution was prepared by taking 5 g of iodine per liter of twice distilled water and dissolving it over a period of several days by periodic shaking. Six ml of the iodine solution (this amount of iodine solution was sufficient to cover the electrodes and bubbler tube completely in the cell which we used) was introduced into the measuring cell. The cell was placed in a thermostat in which it was kept for 15 min at 25°, and connected to the combustion system. Oxygen was then passed through the solution (5 min) and the first measurement of electrical conductivity made; the tap between the measuring cell and the combustion tube was closed, and an oven heated to 1200° fitted onto the tube. Completion of oxidation of the aliquot was followed by means of a rotameter (the level in the rotameter should be at the same position as it was before combustion). When combustion was complete the tap was opened again; the oxygen containing the sulfur dioxide was passed through the measuring cell for 30-40 min, and the electrical conductivity measured again. Measurements were repeated every 10 min. Absorption was regarded as complete when the electrical conductivity of the solution did not change over a period of 10 min.



Relation between increase in electrical conductivity of the iodine solution and the amount of SO_2 absorbed.

After determination of sulfur in one sample of tungsten, standard zinc sulfate solution was added to an equal aliquot of sample and the total amount of sulfur determined. The results obtained are given in Table 1. They show that the method gives satisfactory results.

The method suggested permits determination of $1 \cdot 10^{-4}$ % of sulfur in tungsten with reasonable accuracy.

During oxidation of molybdenum, molybdenum trioxide is formed; the latter completely evaporates at the combustion temperature and blocks up the tube. Consequently, before combustion, it is necessary to add zinc oxide which forms a sparingly volatile compound with molybdenum trioxide. When insufficient zinc oxide is added the readily fusible ternary compound of zinc oxide with quartz and molybdenum trioxide is formed, as a result of which the combustion tube becomes useless (fuses). Zinc oxide should therefore be added in a 4-5 fold excess. The boiling point of molybdenum trioxide is about 1160°, as a result of which the sublimation rate is high at 1200° and the trioxide does not succeed in reacting with the zinc oxide. To avoid this phenomenon, the oven temperature was gradually raised from 900 to 1200°. The remaining details of the method for the determination of sulfur in molybdenum are the same as those used for determination of sulfur in tungsten.

TABLE 1. Determination of Sulfur in Tungsten Metal after Addition of $ZnSO_4$. (The following sulfur contents were found for the W taken: $1.4 \cdot 10^{-4}$; $1.6 \cdot 10^{-4}$; $1.1 \cdot 10^{-4}$; $1.2 \cdot 10^{-4}$; $1.5 \cdot 10^{-4}$% S; mean value $1.4 \cdot 10^{-4}$% S)

Sample	S content (g) in an aliquot $\times 10^{-6}$	S added in (g) $\times 10^{-6}$	Amount of S that should be present (%) $\times 10^{-4}$	S found (%) $\times 10^{-4}$	Deviation (%) $\times 10^{-5}$	Error (%), relative
W + $ZnSO_4$	3.5	2	2.2	1.7	−5	−22.7
W + $ZnSO_4$	3.7	2	2.1	2.2	+1	+ 4.7
W + $ZnSO_4$	4.1	2	2.0	2.3	+3	+13
W + $ZnSO_4$	4.3	2	2.0	1.9	−1	− 5

It follows from Table 2 that the relative error is about 20%. The accuracy for the determination of sulfur in molybdenum is lower than in the case of tungsten, and is strongly dependent on the quality of the zinc oxide. Finally we analyzed two batches of molybdenum for their sulfur content. The amount found in the first bath was $3 \cdot 10^{-5}$; $3 \cdot 10^{-5}$; $1 \cdot 10^{-5}$; $5 \cdot 10^{-5}$% S, while in the second it was $5 \cdot 10^{-5}$% S.

The sulfur content of molybdenum samples analyzed was less than $1 \cdot 10^{-4}$, and in some cases was within the limits of experimental error.

TABLE 2. Determination of Sulfur in Molybdenum Metal (The following sulfur contents were found for the W taken: $4 \cdot 10^{-5}$; $2 \cdot 10^{-5}$; $2 \cdot 10^{-5}$; $6 \cdot 10^{-5}$; $6 \cdot 10^{-5}$; $3 \cdot 10^{-5}$; $4 \cdot 10^{-5}$% S; mean value $4 \cdot 10^{-5}$% S)

Sample	Sulfur content (g) × 10^{-6}	S added (g) × 10^{-6}	S content (%) × 10^{-4}	S found (%) × 10^{-4}	Deviation %	Error (%), relative
MO – 89 + $ZnSO_4$	0.9	2	1.3	1.4	$+1 \cdot 10^{-5}$	+7.7
MO – 89 + $ZnSO_4$	1.2	2	1	0.9	$-1 \cdot 10^{-5}$	−10

SUMMARY

Methods have been developed for the determination of sulfur ($1 \cdot 10^{-4}$ %) in tungsten and molybdenum with a relative error not greater than 20%.

The sulfur dioxide formed is absorbed with a saturated aqueous solution of iodine.

The concentration of the ions formed is determined by electrical conductivity measurements. The sensitivity of the method is 0.2-0.3 μg sulfur.

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DETERMINATION OF ETHYLENEDIAMINETETRACETIC ACID IN SOLUTIONS OF METAL COMPLEXONATES

V. V. Starostin

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 620-622, September-October, 1961
Original article submitted November 1, 1960

Determination of free ethylenediaminetetracetic acid (EDTA) is readily carried out; methods for determining EDTA combined with metal ions which have been described in the literature [1-3] cannot be used universally and are difficult; some of these methods require expensive and not readily available apparatus for measuring optical density in the ultraviolet.

We have developed a simple titrimetric method for the determination of EDTA in solutions containing the complexonates (the ethylenediaminetetracetates) of Fe^{III}, Fe^{II}, Al, Cu^{II}, Ni, Mn^{II}, Cr^{III}, Mg, and Ca which is based on the substitution of the metals from their complexonates by trivalent bismuth which forms a complexonate which dissociates to a lesser extent:

$$[MeEDTA]^{4-n} + Bi^{3+} \rightleftharpoons [BiEDTA]^{-} + Me^{n+}$$

Calculation shows that the equilibrium of this reaction is shifted almost completely toward the right hand side when pK_{MeEDTA} is less than pH_{BiEDTA}, if only by 3 units.

Bismuth complexonate is very stable in acid media; apparently, pK_{BiEDTA} is close to 25. Of the complexonates of the metals listed above, iron (III) and chromium (III) complexonates (pH = 25.0 and about 24 respectively) will not react with excess Bi^{3+} ions. Excess bismuth ions can be back titrated with solution of sodium ethylenediaminetetracetate (EDTA-Na) in an acid medium in the presence of xylenol orange [4, 5] or pyrocatechol violet [2].*

TABLE 1. Determination of EDTA in Solutions Containing Various Metal Ions

Metal (10 mg taken)	EDTA, mg		Error, % (relative)
	taken	found	
Fe^{II}	14,25	14,25	0,0
Fe^{III}	14,25	14,20	—0,3
Al	14,25	14,30	+0,3
Ni	14,25	14,25	0,0
Cu	14,25	14,15	—0,7
Fe^{II} + Fe^{III}	8,8	8,7	—1,1
+ Al + Cu + Ni +	14,25	14,2	—0,3
+ Mn^{II} + Ca +	17,0	16,9	—0,6
+ Mg	28,5	28,3	—0,8
(10 mg each)			

In the work described here we used 0.01 M solutions of $Bi(NO_3)_3$ and EDTA-Na. Xylenol orange was used as indicator.

It was established that in an acid medium (pH about 1) the reaction indicated above proceeds almost quantitatively in the cold in approximately 20 min, and on boiling in 1 min, for all the metal complexonates apart from those of iron (III) and chromium (III). Many complexonates react almost instantaneously.

In the presence of a reducing agent (ascorbic acid) ferric complexonate breaks down to form bismuth complexonate and Fe^{2+} ions. Under these conditions, chromium (III) complexonate hardly interacts at all with bismuth ions. Excess Bi^{3+} was backtitrated with EDTA-Na solution at pH 1-1.5; the color change of the indicator from raspberry to yellow was readily observable.

Experiments showed that EDTA can be determined with satisfactory accuracy even in the presence of large amounts of ions of various metals (Table 1).

The method recommended for the determination of EDTA is described below.

An aliquot of test solution containing 30-60 mg EDTA is introduced into a titration flask and acidified with 5 ml of $HClO_4$ (1:1). After adding 15-25 ml of 0.01 M $Bi(NO_3)_3$ solution the solution is heated to 90-100°. Ascorbic

* Presumably hematoxylin and gallein [6] could also be used for this purpose.

acid is added (0.6-1.0 g) and the solution allowed to stand for 10 min without heating; it is then diluted to about 100 ml with distilled water. A few drops of xylenol orange solution is added and excess bismuth titrated with 0.01 M EDTA-Na solution until the color changes from raspberry to yellow.

S^{2-} ions interfere since they form an insoluble sulfide with bismuth, accordingly they should be removed, e.g., by precipitation with $CuSO_4$.

For determination of EDTA combined with chromium (III) we used a well-known photometric method (measurement of the optical density of solutions of the violet chromium (III) complexonate at 550 mμ) [7, 8]. The pH of the solution being analyzed is adjusted to 3.5-4 according to universal indicator paper by addition of ammonia or sulfuric acid; in order to stabilize the solution EDTA-Na (25 mg/ml) was introduced in addition. The presence of free Cr^{3+} ions in solution, in addition to the chromium complexonate, does not lead to high results, since EDTA-Na and Cr^{3+} react very slowly in the cold. The colored complexonates of copper and nickel, as long as their contents are not too high (Cu, Ni : Cr ≤ 2), do not interfere with the determination since they absorb light strongly at other wavelengths.

Interference from large amounts of iron (III) complexonate is eliminated by addition of a strong reducing agent, e.g., sodium hydrosulfite; should elemental sulfur separate out, the solution is filtered through a fine filter paper.

The chromium complexonate concentration of a sample is determined by means of a calibration curve.

Table 2 contains results of the determination of EDTA in the presence of chromium (III) and other metals.

TABLE 2. Determination of EDTA Combined with Metal Ions

EDTA introduced into the solution,* g/liter	EDTA found in solution, g/liter			Error, % relative
	combined with chromium (photometric method)	combined with other metals (backtitration of excess bismuth)	Total	
1.00	0.63	0.38	1.01	+1.0
3.50	0.73	2.76	3.49	−0.3

*The solution contained 1 g each of Fe and Al per liter; 0.5 g each of Mn, Ca, and Mg per liter; 0.1-0.15 g per liter of Cr; 0.1 g each of Cu and Ni per liter, in the form of their sulfates.

In conclusion the author would like to thank V. F. Luk'yanov for the valuable advice given in the course of this work.

SUMMARY

A titrimetric method is suggested for the determination of ethylenediaminetetracetic acid in the presence of the most common metal ions; it is based on back titration of excess bismuth ions with EDTA-Na in an acid medium in the presence of xylenol orange.

EDTA combined with chromium (III) is determined by measuring the optical density of solutions of chromium (III) complexonate.

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QUANTITATIVE DETERMINATION OF SOME IMPURITIES IN TITANIUM TETRACHLORIDE BY INFRARED SPECTROSCOPY

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 623-626, September-October, 1961
Original article submitted April 18, 1960

Titanium tetrachloride used for metallurgical purposes should be purified as much as possible from all impurities it may contain. In order to organize and improve a purification technique it is essential to have methods for the quantitative determination of compounds which contaminate titanium tetrachloride. In work carried out earlier we demonstrated the possibility and expediency of using infrared absorption spectroscopy for the determination of such impurities as $TiOCl_2$, $VOCl_3$, HCl, C_6Cl_6, $COCl_2$, CO_2, CCl_3COCl [1-2] in titanium tetrachloride. The work described in the present article is a continuation of the study of the molecular nature of the impurities in technical titanium tetrachloride, and is devoted to development of quantitative methods for their determination.

Determination of thionyl chloride. An absorption band with $\nu = 1241$ cm^{-1} is observed in the infrared absorption spectrum of technical titanium tetrachloride and in that of some cases of purified titanium tetrachloride. As experiment has shown, this band belongs to thionyl chloride and corresponds to the valence vibration of the S=O group [3].

The band at $\nu = 1241$ cm^{-1} could be chosen as an analytical band for the quantitative determination of thionyl chloride in titanium tetrachloride. However, it must be borne in mind that determination based on this band is possible only when the titanium tetrachloride does not contain appreciable amounts of such impurities as silicon tetrachloride with an absorption band at $\nu = 1222$ cm^{-1} and phosphorus oxychloride with a band at $\nu = 1226$ cm^{-1} and $\nu = 1264$ cm^{-1}, as well as thionyl chloride. Accordingly, infrared spectroscopy can be expediently used for the determination of the thionyl chloride concentration of purified titanium tetrachloride which contains only very small amounts of silicon tetrachloride and phosphorus oxychloride.

We constructed a calibration curve relating optical density to the concentration of the impurity in standard solutions [4]. For this purpose, the absorption spectra of solutions with the following concentrations were taken: 0.005, 0.01, 0.02, 0.037, and 0.05%. As Fig. 1 shows, the calibration curve is linear; accordingly, the solutions conform to Beer's law over the concentration range examined. Each point on the curve is the mean of three measurements. The absorption coefficient calculated from the curve is equal to $K = 150$ cm^{-1} (when the concentration is expressed in % wt.) or $K = 1040$ liter/mole cm (concentration expressed in mole/liter/cm.

Thus in order to determine thionyl chloride in titanium tetrachloride, it is necessary to measure the optical density at the maximum of the band $\nu = 1241$ cm^{-1}, and, knowing the coefficient, to calculate the concentration required by means of the formula:

$$c = D/Kd,$$

where c is the concentration, D is the optical density, and d is the path length.

The sensitivity of the determination is $1 \cdot 10^{-4}$% (wt.). The relative experimental error does not exceed 3-7%.

Determination of carbon disulfide. During a study of the infrared spectra of many samples of technical titanium tetrachloride, and intense band at $\nu = 1520$ cm^{-1} was observed; this was shown experimentally to belong to carbon disulfide. This band can be used for analytical purposes since it is almost always free from overlapping by the absorption bands of other impurities and from those of titanium tetrachloride itself. Carbon disulfide is miscible with titanium tetrachloride in all proportions [5] and does not interact with it. This is confirmed spectroscopically, since the absorption band of pure carbon disulfide differs very little from the band observed in the spectrum of a solution of this compound in titanium tetrachloride.

For quantitative determination of carbon disulfide, a calibration curve (Fig. 2) was constructed using standard solution with the following concentrations: 0.0011; 0.0055; 0.0108; 0.0205 and 0.0303% (wt.). Each point on the curve is the mean of three measurements. The absorption coefficient determined from the curve is given by K = 780 cm^{-1} or K = 3450 liter/mole cm.

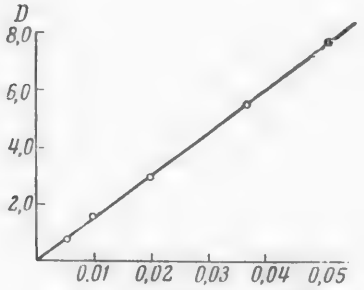

Fig. 1. Calibration curve for the determination of $SOCl_2$ in $TiCl_4$ on the basis of the band at ν = 1241 cm^{-1}.

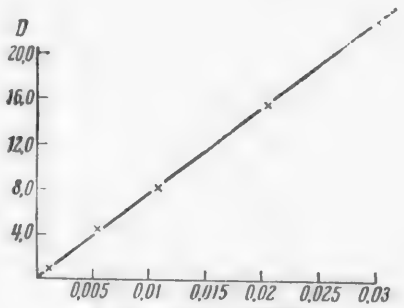

Fig. 2. Calibration curve for the determination of CS_2 in $TiCl_4$ on the basis of the band at ν = 1520 cm^{-1}.

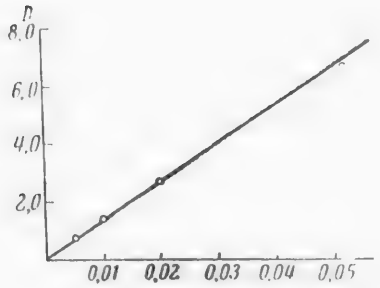

Fig. 3. Calibration curve for the determination of $POCl_3$ in $TiCl_4$ on the basis of the band at ν = 1226 cm^{-1}.

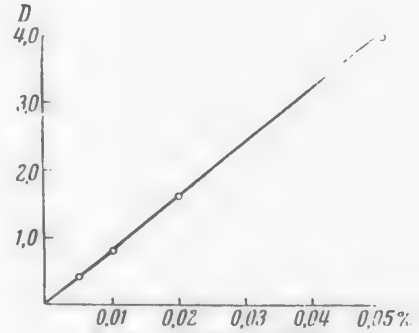

Fig. 4. Calibration curve for the determination of $POCl_3$ in $TiCl_4$ on the basis of the band at ν = 1264 cm^{-1}.

The sensitivity of the determination is $7 \cdot 10^{-6}$%; the relative experimental error does not exceed 3-7%.

Determination of phosphorus oxychloride. Two absorption bands with ν = 1226 cm^{-1} and ν = 1264 cm^{-1} were detected in the spectra of some samples of technical titanium tetrachloride. Chemical analysis of titanium tetrachloride showed the presence of small amounts of phosphorus. Experiments showed that the same two bands are observed in the infrared absorption spectra of a solution of phosphorus oxychloride in titanium tetrachloride. One absorption band at ν = 1295 cm^{-1} is observed in the spectrum of pure phosphorus oxychloride. This band is absent in the spectrum of a solution of phosphorus oxychloride in titanium tetrachloride while the other two bands at ν = 1226 cm^{-1} and ν = 1264 cm^{-1} appear. This testifies to an interaction between phosphorus oxychloride and titanium tetrachloride. There are published references [6-7] to the fact that on adding phosphorus oxychloride to titanium tetrachloride, the compound $POCl_3 \cdot TiCl_4$ is formed; this compound is limitingly soluble in titanium tetrachloride. Accordingly, the two bands observed at ν = 1226 cm^{-1} and ν = 1264 cm^{-1} can, presumably, be ascribed to the complex $POCl_3 \cdot TiCl_4$. It should be pointed out that the boiling point of this compound is 140°, which excludes the practical use of fractional distillation for purifying titanium tetrachloride (b. p. 136°) from phosphorus oxychloride. Both the bands with ν = 1226 cm^{-1} and ν = 1264 cm^{-1} can be used as analytical bands; these bands can be used for quantitative determination in those cases where the titanium tetrachloride only contains negligible amounts of such impurities as silicon tetrachloride and thionyl chloride. Analysis of technical titanium tetrachloride for its phosphorus oxychloride content is best carried out on the basis of the band at ν = 1264 cm^{-1}, which is more free from overlapping by other bands.

Standard solutions with varying contents of phosphorus oxychloride were prepared for the quantitative determination of the latter: 0.005; 0.010; 0.020; 0.051 % (wt.). Calibration curves constructed for the two analytical bands are shown in Figs. 3 and 4. The absorption coefficient for the band at $\nu = 1266$ cm^{-1}, as determined from the curve and calculated on the basis of the $POCl_3$ molecule is 80 cm^{-1} or 715 liter/mole cm. The absorption coefficient for the band at $\nu = 1264$ cm^{-1} is equal to 139 cm^{-1} or 1250 liter/mole cm.

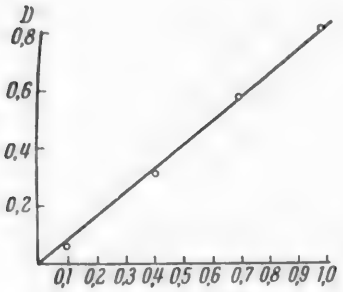

Fig. 5. Calibration curve for the determination of $SiCl_4$ in $TiCl_4$ on the basis of the band at 1222 cm^{-1}.

Knowing the absorption coefficient, it is possible to determine the phosphorus oxychloride concentration on the basis of both bands and to take the mean. In the case of band overlap it is necessary to choose the one more free from overlapping.

The sensitivity of determination according to the band at $\nu = 1226$ cm^{-1} is $1.6 \cdot 10^{-4}$ %, while according to the band at $\nu = 1264$ cm^{-1} it is $1 \cdot 10^{-4}$ %. The experimental error does not exceed 3-7% (relative).

Determination of silicon tetrachloride. Silicon is usually determined in titanium tetrachloride by emission spectrographic analysis. This method requires careful preparation of samples, and, at high silicon contents of the titanium tetrachloride (> 0.1%) gives a large error. It became necessary therefore to develop infrared spectroscopic method for the determination of silicon tetrachloride in titanium tetrachloride. This method permits the reproducibility of the results, and the accuracy with which silicon can be determined in technical titanium tetrachloride to be improved. In addition, the infrared method makes it possible to develop continuous methods for analyzing titanium tetrachloride for its content of this impurity. Titanium tetrachloride exhibits absorption bands in the far infrared and is transparent over a wide frequency range. This means that it is possible to work with long path lengths and opens up possibilities of designing apparatus for continuous control of plant streams. Continuous determination of the silicon concentration of titanium tetrachloride during its fractional distillation would permit the fractionation column to be completely automated.

Impurity	Absorption band, cm^{-1}	Absorption coefficient		Sensitivity % (wt.)	Spectral slit width, cm^{-1}
		cm^{-1}	liter / mole cm		
Thionyl chloride $SOCl_2$	1241	150	1040	$1 \cdot 10^{-4}$	6.6
Carbon disulfide CS_2	1520	780	3450	$7 \cdot 10^{-6}$	8.9
Phosphorus oxychloride $POCl_3$	1226	80	715	$1.6 \cdot 10^{-4}$	6.6
Silicon tetrachloride	1264	139	1250	$1 \cdot 10^{-4}$	6.6
Silicon tetrachloride $SiCl_4$	1222	0.807	8.0	$2 \cdot 10^{-2}$	

Silicon tetrachloride has the following fundamental vibration absorption bands: 150; 220; 425; 607 cm^{-1} [8]. The band at $\nu = 607$ cm^{-1} can be observed when a KBr prism is used. Analysis of titanium tetrachloride for most of the impurities it contains is carried out over the region in which NaCl and LiF prisms are transparent. Work with a spectrometer fitted with a KBr prism presents certain experimental difficulties and requires additional study. All this complicates control of the quality of titanium tetrachloride under production conditions. It should also be pointed out that prism resetting also takes some time. We accordingly chose the band at 1222 cm^{-1} which belongs, apparently, to the first overtone of the frequency at $\nu = 607$ cm^{-1}. The sensitivity of a determination based on this band is low, but it is still sufficient for the determination of silicon in technical titanium tetrachloride. For constructing a calibration curve (Fig. 5) standard solutions of silicon tetrachloride in titanium tetrachloride were prepared with the following concentrations: 0.10; 0.40; 0.70 and 0.99% (wt.). Each point on the curve is the mean of three measurements. The absorption coefficient found from the curve was K = 0.807 cm^{-1} or K = 8.0 liter/mole cm.

During determination of silicon tetrachloride one must take into account the possibility of overlapping from the bands of titanium oxychloride $\nu = 1184$ cm^{-1}, thionyl chloride $\nu = 1241$ cm^{-1}, and phosphorus oxychloride

ν = 1226 cm^{-1}. The effect of such overlapping, however, only shows up at relatively high concentrations of the impurities mentioned. The titanium oxychloride concentration of technical titanium tetrachloride does not usually exceed 0.2%, while that of thionyl chloride does not exceed 0.01%, and that of phosphorus oxychloride 0.005%; in such cases band overlapping does not show an appreciable effect on the determination of silicon tetrachloride content.

The sensitivity of determination is 0.02%. The error does not exceed 3-7% (relative).

The method developed has a number of advantages over chemical and emission spectrographic methods. They include: a shorter time for carrying out a determination; direct use of the titanium tetrachloride for analysis without preliminary hydrolysis; the possibility of designing apparatus for continuous determination of silicon in titanium tetrachloride; better reproducibility of the results.

The most important data obtained during development of techniques for determining these impurities in titanium tetrachloride by means of an IKS-12 spectrometer fitted with a NaCl prism, are given in the table.

SUMMARY

New impurities have been detected in titanium tetrachloride; they include thionyl chloride, phosphorus oxychloride, and carbon disulfide. Methods have been developed for the quantitative determinations of $SOCl_2$, $POCl_3$, CS_2, and $SiCl_4$ in titanium tetrachloride by infrared spectroscopy.

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SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN NIOBIUM

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 627-630,
September-October, 1961
Original article submitted March 11, 1960

The main difficulty which arises during the spectrographic determination of impurities, in particular, iron, silicon, titanium, tantalum, and lead, in niobium metal is the preparation of reliable standards. Since niobium metal readily oxidizes in air at 600-700° it is expedient to prepare standards and samples in the form of niobium pentoxide. Published spectrographic methods only deal with the determination of tantalum and titanium [1, 7] and readily volatile lead, tin, cadmium, bismuth, and antimony [2] in niobium pentoxide. After the work described here had been completed a brief communication appeared on the use of the spectrographic method for the determination of a number of elements including iron, silicon, titanium, and tantalum [3] in niobium pentoxide. Unfortunately no information is given in this paper on the sensitivity and accuracy of the determination.

Choice of conditions. Results obtained. The most convenient light source for the spectrographic determination of impurities in powders at a high sensitivity level is a dc arc. Accordingly, during the simultaneous determination of iron, silicon, titanium, tantalum, and lead in niobium pentoxide, the spectra were excited in a dc arc. In order to prevent samples being thrown out of the electrode crater, the pentoxide was mixed beforehand with carbon powder (in the proportion of 2:1), while the current was kept at 6.5 amps for 15 sec during the initial period of arc burning, and was then raised for 12 amps. Excitation of the spectra at a low current, in addition, significantly increased the sensitivity and reproducibility of the determination of lead. The total exposure time was 2 min. Samples weighing 30 mg were placed in the carbon electrode crater which was 4 mm in diameter and 3mm deep. The lower electrode containing the sample served as the anode, while a carbon rod 6 mm in diameter was used as cathode. The spectra were photographed on a large Hilger quartz spectrograph using "diapositive" plates with a sensitivity of 0.25 GOST unit and "spectrographic type 1" with a sensitivity of 0.7 GOST unit. The spectrograph slit was illuminated with a one lens condenser.

The spectrum excitation conditions were chosen on the basis of study of the burning out curves obtained at arc current values of 10, 12, and 15 amps (at i = 12 amps in Fig. 1). Burning out curves for tantalum, titanium, silicon, and niobium on adding carbon powder to the sample, have, as a rule, two maxima each. We suggest that these maxima are determined by the formation of carbides during arc burning. It was established on the basis of the burning out curves that all the test impurities evaporated almost completely in 2 min when the current had values of 12 and 15 amps. However, for i = 15 amps there is observed a fairly intense background; it is better therefore to work at a current of 12 amps.

The internal standard method was adopted to improve the reproducibility of the determinations. Cobalt, which was added to standards and samples to a concentration of $8 \cdot 10^{-2}$ %, was used as an internal standard during silicon and iron determination. Niobium lines were used as reference lines for determination of titanium and tantalum. The analytical lines and the concentration ranges studied are given in Table 1. Typical calibration curves constructed within the coordinates $\log C - \Delta S$ are shown in Fig. 2.

Over the concentration ranges indicated, the curves are linear. By converting from blackening to intensity, iron, silicon, titanium, and lead can be determined with a sensitivity of $1 \cdot 10^{-3}$%, and tantalum with a sensitivity of $3 \cdot 10^{-2}$%.

The reproducibility of a single determination, which is characterized by the mean square error, amounts to 10% for tantalum and titanium, 11% for silicon, 13% for lead, and 16% for iron.

The reliability of the method was evaluated from the analytical results for samples to which known amounts of the test impurities had been added (Table 2). The figures given in the table testify to the completely satisfactory accuracy of the method developed.

Up to 1% of "third elements:" iron, silicon, lead, and calcium does not affect the sensitivity and accuracy of determination.

Preparation of spectrographically pure niobium pentoxide and preparation of standards. In order to obtain pure niobium pentoxide for preparing standards we have developed a method in which niobium is separated from tantalum on the basis of the difference in the extractability of their fluoride complexes with cyclohexanone [4-6].

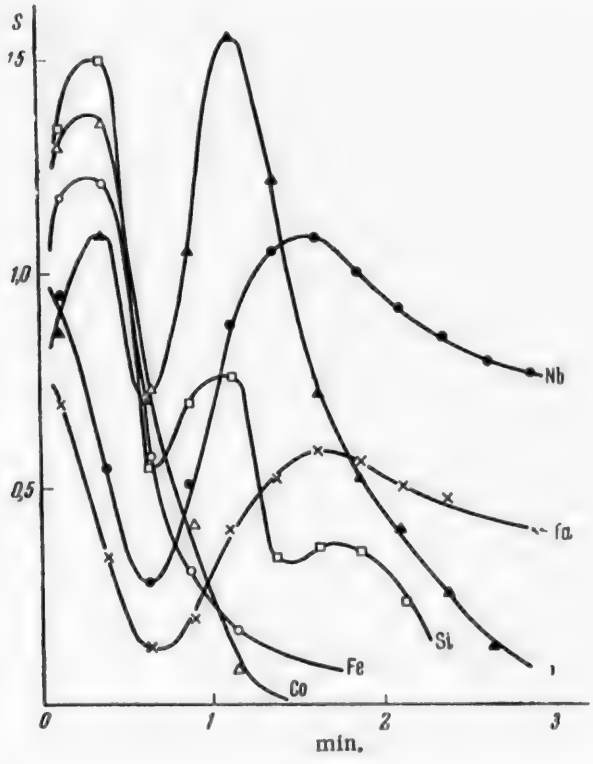

Fig. 1.

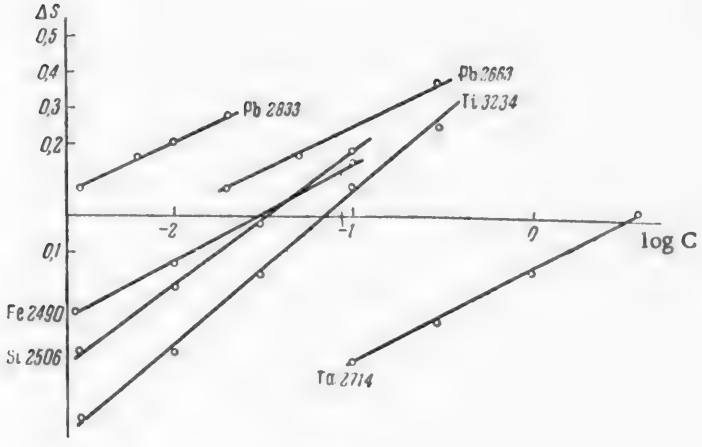

Fig. 2.

Niobium is separated from titanium and other impurities by converting niobic acid with hydrogen peroxide and ammonia in the presence of sodium ethylenediaminetetracetate into ammonium peroxyniobate $(NH_4)_3NbO_8$.

Under these conditions the impurities remain in solution. On heating, ammonium peroxyniobate readily changes into niobium pentoxide whose tantalum content is less than $1 \cdot 10^{-4}$%, while its titanium, iron, silicon, and lead contents do not exceed $1 \cdot 10^{-3}$%.

For preparing the fluoride solution, technical niobium, in the form of turnings, is placed in a platinum beaker and dissolved in a mixture of hydrofluoric and nitric acids. The earth element acids are precipitated from solution with ammonia, the precipitate is filtered off and washed with water to free it from nitrate ions. The precipitate is then dissolved in 40% hydrofluoric acid, the acidity is adjusted to 0.8-1 M and the tantalum extracted with cyclohexanone. After the phases have separated, the tantalum which is in the extract is precipitated with ammonia, filtered off, calcined, and weighed. The tantalum content of the precipitates is determined spectrographically. Tantalum is removed from a solution containing 200 g of niobium, as the results in Table 3 show, after four extractions.

TABLE 1

Test elements	Analytical lines, A	Reference lines, A	Test concentration range, %
Iron	Fe 2490.64	Co 2528.97	$3 \cdot 10^{-3} - 1 \cdot 10^{-1}$
Silicon	Si 2506.89	Co 2528. 97	$3 \cdot 10^{-3} - 1 \cdot 10^{-1}$
Titanium	Ti 3234.52	Nb 3248.86	$3 \cdot 10^{-3} - 3 \cdot 10^{-1}$
Tantalum	Ta 2714.67	Nb 2714.19	0.1 – 3.0
Lead	Pb 2833.07	The background on the right of the analytical line	$3 \cdot 10^{-3} - 3 \cdot 10^{-2}$
	Pb 2663.17	The same	$3 \cdot 10^{-2} - 3 \cdot 10^{-1}$

TABLE 2

Sample No.	Test elements									
	titanium		silicon		iron		tantalum		lead	
	Introduced, %	Found, %	Introduced, %	Found, %	Introduced, %	Found, %	Introduced, %	Found, %	Introduced, %	Found, %
1	$6.5 \cdot 10^{-3}$	$7.2 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	–	–		
2	$2.0 \cdot 10^{-2}$	$1.8 \cdot 10^{-2}$	$6.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$	$6.5 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$	–	–	$6.5 \cdot 10^{-3}$	$6.5 \cdot 10^{-3}$
3	$6.5 \cdot 10^{-2}$	$6.6 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	0.60	0.54	$5.0 \cdot 10^{-2}$	$4.0 \cdot 10^{-2}$
4	0.20	0.25	$6.5 \cdot 10^{-2}$	$7.2 \cdot 10^{-2}$	$6.5 \cdot 10^{-2}$	$6.6 \cdot 10^{-2}$	2.0	1.8	0.2	0.25

TABLE 3

Extraction	Amount of Nb and Ta in the extracts, mg	Ta content according to spectrographic analysis of the extracts, %	Amount of Ta extracted, mg
I	1820	35	637
II	1450	3.6	52.7
III	1000	0.7	7.0
IV	320	0.1	0.32

Niobium, which is contained in the aqueous phase, is precipitated with niobium, the precipitate is filtered off and washed with hot water. The precipitate which has been washed free of fluoride ions is transferred to a beaker, 100 ml of a 50% solution of ammonium ethylenediaminetetracetate and 250-300 ml of 25% ammonia solution are added, the mixture is cooled and 30% hydrogen peroxide added gradually with stirring until a coarse crystalline precipitate of ammonium peroxyniobate is formed. Solution plus precipitate are cooled for 1-2 hr, the precipitate is then filtered off and washed 2-3 times with small portions of 25% ammonia solution. The precipitate is again transferred to a beaker and dissolved in 200 ml of 50% tartaric acid heated to 50-70°, and the insoluble residue filtered off. Four-hundred ml of 30% hydrogen peroxide is added to the cooled solution and ammonium peroxyniobate precipitated with 25% ammonia solution. The precipitate is filtered off, washed with 25% ammonia solution, and dried in a vacuum desiccator. Ammonium peroxyniobate decomposes at 70-72° to form niobium pentoxide which is then calcined at 700-800°.

Standards are prepared on the basis of niobium pentoxide to which are added calculated amounts of tantalum, iron, silicon, titanium, and lead oxides, cobalt oxide being added as the internal standard. The mixture is placed in a platinum basin and ground for one hour. The remaining standards are prepared by diluting the original standard with the base and adding the internal standard.

SUMMARY

Methods have been developed for the spectrographic determination of iron, silicon, titanium, tantalum, and lead in niobium, and for obtaining highly pure niobium pentoxide which can be used for preparing spectrographic standards.

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DETERMINATION OF TITANIUM IN TITANIUM CARBIDE–NIOBIUM ALLOYS

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 631-634, September-October, 1961
Original article submitted March 24, 1960

Analysis of materials containing niobium, tantalum, and titanium is one of the most difficult problems in analytical chemistry. All known gravimetric methods involving the use of tannin, pyrogallol, acridine, 8-hydroxyquinoline etc. [1-5] require two, and in most cases, three reprecipitations which involves filtering and washing the precipitates. Not only are they tedious and inconvenient to carry out, but, as a number of studies have shown [6], they do not give sufficiently accurate results. The most promising approach would seem to be the direct titrimetric method of determining titanium in the presence of niobium, a method suggested by Winterstein [7], and also by Tomicek et al. [8]. In hydrochloric acid solutions titanium is reduced to its trivalent state by zinc amalgam in the presence of sodium fluoride. Under these conditions niobium is not reduced. According to Tomicek [8], in the presence of 25% tartaric acid, niobium is not reduced by zinc amalgam or amalgamated zinc. Under these conditions titanium is reduced to the trivalent state. Working with mercury presents certain difficulties. Accordingly, metallic cadmium and aluminum are widely used for reducing titanium.

The aim of the work described here was to obtain more accurate information on the reducibility of niobium and titanium by aluminum in the presence of masking agents, to establish the optimum conditions for reducing titanium, and to develop a method for determining titanium in TiC–Nb alloys.

EXPERIMENTAL

Metallic niobium was dissolved in a mixture of hydrofluoric acid with a few drops of concentrated nitric acid; sulfuric acid was then added and the liquid evaporated until SO_3 fumes were evolved. The sulfuric acid solution of niobium was diluted so that the niobium content of 10 ml of solution was not greater than 0.08-0.1 g. A titanium solution of the same concentration was prepared.

In order to study the effect of fluorides on the reduction of niobium in sulfuric-hydrochloric acid solutions by metallic aluminum, the following experiments were carried out. To solutions containing the same amount of niobium was added 20 ml of concentrated sulfuric acid and from 20 to 30 ml of concentrated hydrochloric acid. The volume of the solution was made up to 200 ml with water. Niobium was reduced with metallic aluminum in the presence of varying amounts of sodium or ammonium fluoride, the solution was cooled and the reduced solution titrated with a ferric alum solution in the presence of potassium thiocyanate. The results obtained are given in Table 1. Large amounts of fluorides (Table 1) are necessary to prevent reduction of niobium with metallic aluminum in sulfuric-hydrochloric acids.

It is more convenient to add ammonium fluoride, since it is appreciably more soluble than sodium fluoride; moreover, in the presence of ammonium fluoride sparingly soluble Na_3AlF_6 is not precipitated. The presence of varying amounts of hydrochloric acid in the mixture of sulfuric and hydrochloric acids has almost no effect on the reduction of titanium with metallic aluminum, at the same time, in the presence of hydrochloric acid the amount of niobium reduced increases sharply. Considerably smaller amounts of fluorides are required for preventing reduction of niobium in sulfuric-hydrochloric acid solutions than in hydrochloric acid solutions. Results on the reduction of niobium in sulfuric acid solutions in the presence of ammonium fluoride are given in Table 2. Accordingly, it is possible to prevent reduction of niobium by adding small amounts of ammonium fluoride. The following results were obtained (Table 3) during titration of mixtures of niobium and titanium in a sulfuric acid medium in the presence of ammonium fluoride.

When even small amounts of hydrochloric acid (about 5 ml) are added to sulfuric acid solutions of niobium and titanium salts in the presence of ammonium fluoride, appreciable reduction of niobium occurs. Not only fluorides, but also tartaric, oxalic, and citric acids, and sodium ethylenediaminetetracetate (Table 4) can be used for complexing niobium into a complex which is not reduced by metallic aluminum. On the basis of the results given in Table 4, one can conclude that quadrivalent titanium, in the presence of fluorides, oxalic, citric, and tartaric acids, and sodium ethylenediaminetetracetate can be readily reduced with metallic aluminum to the trivalent state, while quinquevalent niobium is not reduced under these conditions.

TABLE 1. Effect of Fluorides on Reduction of Quinquevalent Niobium with Aluminum in Sulfuric-Hydrochloric Acid Solutions (Niobium taken 0.044 g)

NaF, added, g	Extent to which niobium is reduced	Color of the niobium solution	NH_4F added, g	Extent of reduction	Color of the niobium solution
–	3.7	Black	–	3.7	Black
2	4.2	Brown	2	3.8	Brown
3	4.4	Ditto	6	4.5	Ditto
5	4.7	Yellow	10	4.9	Bright-yellow
7.5	4.8	Bright-yellow	12	4.97	Colorless
10	4.93	Almost colorless	15	4.98	Colorless
15	4.94	Ditto			

TABLE 2. Effect of Fluorides on the Reduction of Niobium in a Sulfuric Acid Medium (0.044 g niobium taken)

NH_4F, added g	Extent to which niobium is reduced
0.2	4.65
0.4	4.88
0.6	5.00
1.0	5.00

TABLE 3. Determination of 0.0884 g of Titanium in a Sulfuric Acid Medium in the Presence of Niobium

Niobium added, g	Ti:Nb ratio	NH_4 added, g	Found, g
0.096	1:1	0.5	0.0886
0.096	1:1	1.0	0.0886
0.144	1:1.5	1.0	0.0887
0.198	1:2	1.5	0.0886

EXPERIMENTAL

0.1-0.2 g of a TiC–Nb alloy is dissolved in 10-15 ml of a HF + HNO_3 mixture. When dissolution is complete the solution is evaporated to a small volume, 10 ml of sulfuric acid is added and the liquid evaporated to the appearance of white SO_3 fumes. After being cooled, the solution is transferred to a 250 ml conical flask; 20-25 ml of concentrated sulfuric acid is added, followed by 1 g of ammonium fluoride or 5-7 g of citric or tartaric acid, the solution is diluted to 100 ml with water and 1.5-2.0 g of metallic aluminum added in individual portions while the solution is continuously cooled. When turbulent liberation of hydrogen in the cold is complete, a stopper with two inlet tubes is fitted into the flask; one is connected to a CO_2 supply while the other serves for leading off the gas. The flask is placed on a hotplate and is boiled until the aluminum has dissolved completely; the solution is then cooled while the CO_2 is passed through it and is rapidly titrated with a ferric alum solution until it has a rose color. The ferric alum solution is standardized against a standard solution of titanium or ferrotitanium.

Should the alloy not dissolved in the HF + HNO_3 mixture, it is fused in a platinum crucible with potassium pyrosulfate. The melt is leached into 20 ml of 30% tartaric or citric acid, the solution is transferred into a conical flask and 20 ml of concentrated sulfuric acid added; the procedure outlined above is then followed.

Titanium carbide alloys containing different amounts of niobium were analyzed by the method suggested using citric acid. Results of parallel determinations are given below:

Sample		Titanium found	
1	3.52	3.44	3.48
2	14.50	14.40	14.42

Sample	Titanium found		
3	28.70	28.82	28.74
4	58.67	58.60	58.67
5	69.55	69.70	69.60

TABLE 4. Effect of Masking Agents on the Reduction of Titanium and Niobium in Sulfuric Acid Solutions by Metallic Aluminum (total volume of solution 200 ml)

Concentrated		Added, g				ml of 0.078 N $NH_4Fe(SO_4)_2$ solution used
H_2SO_4, ml	HCl, ml	citric acid	tartaric acid	oxalic acid	sodium ethylenediaminetetracetate	
			0.088 g titanium taken			
20	—	—	—	—	—	23,30
20	—	2,5	—	—	—	23,35
20	—	5,0	—	—	—	23,30
20	—	7,5	—	—	—	23,25
20	—	10,0	—	—	—	23,35
20	—	—	3,5	—	—	23,4
20	—	—	7,0	—	—	23.35
20	—	—	10,0	—	—	23,30
20	—	—	—	2,0	—	23,35
20	—	—	—	4,0	—	23,30
20	—	—	—	6,0	—	23,35
20	—	—	—	—	5,0	23,40
20	—	—	—	—	10,0	23,45
			0.096 g niobium taken			
20	—	—	2,0	—	—	0,6
20	—	—	3,5	—	—	0,3
20	—	—	7,0	—	—	0,0
10	10	—	7,0	—	—	2,1
20	—	2,5	—	—	—	0,2
20	—	5,0	—	—	—	0,0
10	10	5,0	—	—	—	1,5
20	—	—	—	2,0	—	0,2
20	—	—	—	4,0	—	0,0
20	—	—	—	—	5,0	0,0
20	—	—	—	—	10,0	0,0

SUMMARY

A method has been developed for the titrimetric determination of titanium in titanium–niobium alloys after its reduction with metallic aluminum in the presence of fluorides, oxalic, tartaric, and citric acids or sodium ethylenediaminetetracetate in a sulfuric acid medium. Hydrochloric acid promotes reduction of niobium. The method has been used for the determination of titanium in alloys of titanium carbide and metallic niobium.

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ELEMENTAL-ORGANIC ANALYSIS BY THE "WET COMBUSTION" METHOD

COMMUNICATION 4. DETERMINATION OF CARBON, SILICON, AND ALUMINUM IN POLYMERIC ORGANOALUMINOSILOXANES*

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 635-638, September-October, 1961
Original article submitted October 19, 1960

Existing methods for the analysis of silicoorganic materials which are based on combustion in an oxygen stream, permit determination of carbon, hydrogen, and silicon [2-3], or carbon, hydrogen, silicon, and halogen (or sulfur) [4] on one aliquot. For the analysis of silicoorganic compounds containing metal atoms, however, these methods are not suitable for the determination of both silicon and metal. It is best to use the "wet combustion" method in such cases [5].

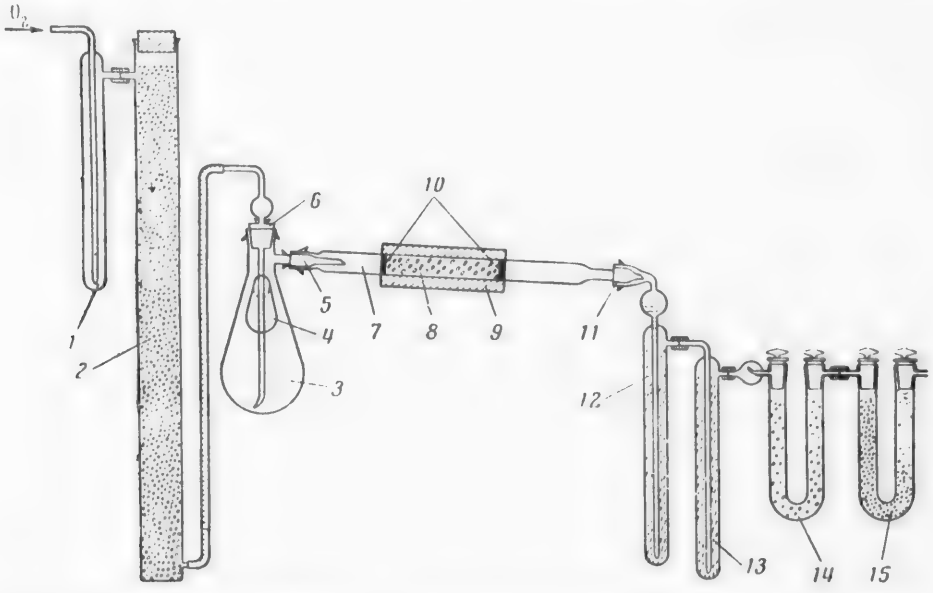

Fig. 1. Wet combustion apparatus. 1) Bubble counter filled with concentrated sulfuric acid; 2) askarite column for purifying the oxygen; 3) reaction flask; 4) side tube, fused into the flask, for introducing chromic acid; 5) ground joint; 6) ground stopper with tube for introducing oxygen; 7) quartz tube (200 ml long, 8-10 mm diameter); 8) catalyst—chromic oxide on pumice; 9) electric oven at 700-750°; 10) loose fitting asbestos plugs; 1)) ground joint; 12) halogen absorber containing pieces of glass rod moistened with an acetic acid solution of hydrazine (pH 6); 13) flask containing pieces of glass rod moistened with concentrated sulfuric acid; 14) tube containing anhydrone; 15) tube containing askarite and anhydrone.

Wet combustion, as a method of breaking down silicoorganic compounds which contain various metals and metalloids, can be used in a very wide variety of cases, since in addition to carbon and silicon, it also permits determination of other elements which remain in the filtrate after removal of the carbon and silicon. Complete oxidation of various polymers is possible by choosing appropriate oxidizing mixtures and decomposition conditions.

* For communication 3, see [1].

** L. N. Karabashkina took part in the experimental work.

Earlier [6], we suggested a method for oxidizing silicoorganic compounds with sulfuric and chromic acids in an oxygen stream for the determination of carbon and silicon, and carbon, nitrogen, and copper or iron in organic compounds containing metals. It was established in the course of the work described in the present article that it is necessary, in order to destroy polymeric organoaluminosiloxanes by the wet combustion method, to heat the test material in concentrated sulfuric acid beforehand. It was obvious that during such treatment the bond $\equiv\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Al}}=$ [7] was broken, and further oxidation of these siloxanes with chromic acid proceeded appreciably more rapidly. The silica formed during this stage was removed from the sulfuric acid by filtration, gelatin solution being added to accelerate filtration. The silicon was then converted into sodium fluorosilicate and determined titrimetrically [8]. Aluminum was determined in the filtrate after removal of silicon. In order to separate aluminum from chromium which is always contained in appreciable amounts in the sulfuric acid solution after combustion, we adopted electrolysis with a mercury cathode [9]. Chromium was thereby held by the mercury, while the aluminum remained in solution. Aluminum was determined titrimetrically with sodium ethylenediaminetetracetate (EDTA-Na) [10]. Carbon was determined gravimetrically as usual.

TABLE 1. Determination of Aluminum

Aliquot of polyphenylaluminosiloxane, mg	Al, mg				
	content of the aliquot	added	total amount	found	difference
89,95	10,97	4,84	15,81	16,01	+0,20
90,64	11,06	2,42	13,48	13,59	+0,11
50,98	6,22	4,84	11,06	11,23	+0,17
50,53	6,14	2,42	8,56	8,52	—0,04
52,25	6,37	2,42	8,79	8,74	—0,05

TABLE 2. Determination of Carbon, Silicon, and Aluminum on One Aliquot

Test material	aliquot, mg	C, %	Si, %	Al, %
Polyethylaluminosiloxane Batch 1	49,10	15,3	15,2	14,6
	50,90	15,5	15,0	14,3
Polyethylaluminosiloxane Batch 9	50,88	16,7	12,2	17,2
	52,58	17,1	11,8	16,9
Polyethylauminosiloxane Batch 21	48,30	15,1	14,0	13,9
	51,70	14,9	13,6	13,8
Polyphenylaluminosiloxane	51,20	35,7	12,0	15,5
	48,55	35,3	12,4	15,3

Since we had no individual polymeric organoaluminosiloxanes at our disposal, we adopted the following procedure in order to establish the accuracy of the determination. Aluminum was determined beforehand by the suggested method (12.2% Al) in technical polyphenylaluminosiloxane. Next, a known volume of aluminum sulfate solution prepared from aluminum metal Mark AB1 was introduced into the reaction flask 3 (Fig. 1), and the liquid evaporated almost to dryness, an aliquot of the siloxane with the known aluminum content was introduced, and oxidation and determination of aluminum carried out as described below. The results obtained are given in Table 1.

The carbon, silicon, and aluminum contents of samples of technical polymeric ethyl- and phenylaluminosiloxanes were determined on one aliquot by the suggested method. It is clear from the results obtained that there is satisfactory agreement between parallel determinations.

EXPERIMENTAL

Into a dry reaction flask 3 (Fig. 1) containing an aliquot of test material is introduced 5 ml of concentrated sulfuric acid,* while through side tube 4 is introduced 1.5-2 ml of chromic acid.** The flask is connected, as shown

* The sulfuric acid is heated beforehand for 40-50 min in order to destroy any possible organic impurities, and then cooled in a flask fitted with a ground glass calcium chloride tube.

** Seventy g of chromium trioxide is dissolved in 100 ml of water and boiled for 3-5 min. The cooled solution is filtered through a glass filter.

in Fig. 1, oxygen is passed through for 2-3 min and weighing tube 15 connected. Without stopping the oxygen flow, the flask is immersed for 10-15 min in a bath heated to 150-160°, and on cooling a small amount of chromic acid is added from side tube 4; liberation of carbon dioxide bubbles is observed during this stage. Oxidation usually proceeds quietly without foaming. When any visible reaction has stopped the flask is again heated at the same temperature for 30 min.

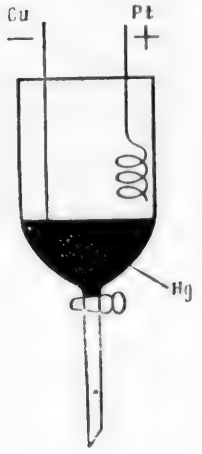

Fig. 2. Electrolytic cell.

The carbon content is determined from the increase in weight of tube 15 filled with askarite following from the absorption of carbon dioxide. Silicon and aluminum are determined in the contents left in reaction flask 3 after combustion. For this purpose the flask is disconnected, the silica adhering to the walls is washed off with water and then filtered off, the silicon is finally determined titrimetrically by a method described earlier [8].

Aluminum is determined as follows. After removal of the silicon, the sexivalent chromium in the filtrate is reduced by heating with a few drops of methanol. The solution is transferred into a 200 ml standard flask, an aliquot of this solution (50 ml) is transferred into an electrolytic cell (Fig. 2) containing 30-40 ml of mercury metal and 50-60 ml of water. The electrodes are connected to a dc current source and electrolysis carried out with a current of 5 amps at a voltage of 22 v over a period of 100-120 min. The colorless solution obtained in syphoned from the electrolytic cell into a conical flask, and the electrolytic cell washed 4-5 times with 5-7 ml lots of water. The solution in the flask is evaporated to a volume of about 50 ml, it is neutralized with 25% alkali solution (using congo red paper), 1 ml of concentrated sulfuric acid and 20 ml of 0.01 M EDTA-Na solution are added and the solution heated to incipient boiling. On cooling, the solution is neutralized with 1 M ammonia solution, and 2-3 ml of the latter added in excess; excess EDTA-Na solution is then rapidly titrated with 0.01 M zinc chloride solution using chromogen black ET-00.* At the end point there is a distinct color change from blue to violet. A control test should be carried out during aluminum determination. For this purpose 5 ml of sulfuric acid is added to 1.5-2 ml of chromic acid, sexivalent chromium is reduced and water is added to bring the volume to 200 ml. Fifty ml of the solution obtained is introduced into the electrolytic cell to remove the chromium, and the solution then taken through all the stages described above.

SUMMARY

A method has been developed for the determination of carbon, silicon, and aluminum in polymeric organoaluminosiloxanes using one aliquot, in which the test material is oxidized with a mixture of chromic and sulfuric acids at 150° in an oxygen stream. Additional complete combustion of possible incomplete combustion products is carried out over chromic oxide heated to 700-750°. Carbon is determined gravimetrically; silicon is determined titrimetrically after conversion of the silica formed into sodium fluosilicate; aluminum is determined complexometrically.

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*100 mg of indicator is carefully mixed with 10 mg of finely ground sodium chloride [10]; this mixture is added on the tip of a microspatula.

DETERMINATION OF FURANE AND TETRAHYDROFURANE COMPOUNDS BY INFRARED SPECTROSCOPY

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 639-642,
September-October, 1961
Original article submitted February 25, 1961

Increasing attention has been given in recent years to the chemistry of furane compounds, including problems relating to catalytic hydrogenation, hydrogenolysis, and alkylation of oxygen-containing heterocyclic compounds. These problems cannot be solved, however, without a well established analytical background. Until recently no methods have been published on the determination of furane compounds containing alkyl radicals in the side chain. We have successfully used gas liquid chromatography for determination of furane, tetrahydrofurane and their homologs [1].

In the work described here an attempt was made to use infrared spectroscopy for determination of furane and tetrahydrofurane compounds. There is already a well developed technique for the determination of methyl and methylene groups on the basis of the intensity of the respective absorption bands in the infrared, in the case of alkanes of normal and branched structure and also for cyclanes [2-5]. A considerably smaller amount of work has been devoted to studies of the structure of the alkyl radical in aromatic and unsaturated compounds, and in organic acids etc. [6-8]. It has been shown in these papers that the intensity of the absorption bands of CH_2- and CH_3- groups in the infrared spectrum is not proportional to the number of the respective groups, and that methods used for determination of alkanes should be developed further so that they can be applied for determination of compounds in the classes indicated above.

The work described here is devoted to a study of the possibility of using the method developed for alkenes to the determination of the number of methyl and methylene groups in the alkyl radicals of furane and tetrahydrofurane compounds.

Taking into account the advantages and disadvantages of the various methods, we settled on Jones' method [4] which permits the number of CH_2- and CH_3- groups to be determined reasonably accurately and most rapidly on the basis of infrared spectra.

We obtained the infrared absorption spectrum in the region 2800-3100 cm^{-1} for each representative of both the furane and tetrahydrofurane series on a double beam UR-10 infrared spectrophotometer. The compounds were examined in CCl_4 solution at a concentration of 0.1-0.03M in constant path length cells. The path lengths were 1.05 0.25 mμ. The spectral slit width was 2.5 cm^{-1}. At this slit width the error introduced into the measurement of the value of peak intensity as a result of the terminal slit width, was insignificant, and as calculations made by Ramsey's method showed, decreased the value of the intensity by less than 20%. At the concentrations we used the solutions conform well to Beer's law. Calculations were made using the formula:

$$I = D_{max}/Cd$$

where D_{max} is the optical density at maximum absorption; C is the concentration of the test material, M; $\underline{d}$ is the path length, cm; I is the intensity, which is proportional to the absorption coefficient. For analytical purposes we used the absorption bands of the asymetrical vibration of the CH_2- groups and the double degenerated vibrations of the CH_3- groups. The relation of the bands in the infrared spectra was established according to the data in the paper by Shappard and Simpson [9], which has been confirmed in subsequent articles [2-4, 10, 11]. Since the absorption bands of CH_2- and CH_3- groups partially overlap, in a small number of cases the complex contour of the absorption bands was resolved into its components; this was made considerably easier by the fact that the absorption bands had a contour which was symmetrical and comparatively well described by dispersion formulas.

Table 1 contains the absorption band frequencies of the antisymmetric vibration of the CH_2-group and the twice degenerated vibration of the CH_3-group for standard compounds of the furane and tetrahydrofurane series. All the compounds used as standards were carefully purified by distillation in a high efficiency fractional distillation column. The purity of the preparations were checked by gas liquid chromatography. Their constants are given in Table 2. The position of the absorption bands of the methyl and methylene groups for all the compounds, apart from α-methylfurane and α-ethylfurane, corresponds to collected published data 2962 ± 10 cm^{-1} and 2926 ± 10 cm^{-1} [12].

TABLE 1. Position of the Absorption Bands of the Antisymmetric Vibration of the Methylene Group and of the Twice Degenerated Vibration of the Methyl Group

Compound	Absorption band frequency, cm^{-1}		Compound	Absorption band frequency, cm^{-1}	
α-Methylfurane	2956	2926	α-n-Propyltetrahydrofurane	2964	2934
α-Ethylfurane	2985	2940	α-Isobutyltetrahydrofurane	2962	2931
α-n-Propylfurane	2964	2935	α-Propyl-β-ethyltetrahydrofurane	2964	2934
α-n-Butylfurane	2961	2933	α-Ethyl-α'-propyltetrahydrofurane	2965	2934
α-n-Amylfurane	2960	2932	α-Methyl-α'-propyltetrahydrofurane	2966	2933
α-Methyltetrahydrofurane	2974	–		CH_3	CH_3
α-Ethyltetrahydrofurane	2967	2937			

TABLE 2. Physicochemical Properties of Standard Compounds

Compound	t° b. p.°/mm	d^{20}_4	$n^{20}D$
α-Methylfurane	63-64	0.3188	1.4340
α-Ethylfurane	92-93	0.9020	1.4415
α-n-Propylfurane	114-115	0.8308	1.4400
α-n-Butylfurane	137-138	–	1.4460
α-n-Amylfurane	163-164	–	1.4472
α-Methyltetrahydrofurane	78-79	0.8563	1.4070
α-Ethyltetrahydrofurane	107-107	0.8550	1.4160
α-n-Propyltetrahydrofurane	132-133	0.8562	1.4226
α-Isobutyltetrahydrofurane	149-150	0.8485	1.4262
α-Propyl-β-ethyltetrahydrofurane	68-70 [13]	0.8558	1.4380
α-Methyl-α'-propyltetrahydrofurane	144-145 [5]	0.8507	1.4240
α-Ethyl-α'-propyltetrahydrofurane	90-92 [63]	0.8516	1.4295

An appreciable shift in the position of the absorption bands was only observed in the case of α-ethylfurane and -methylfurane, while splitting of the absorption band into its components was also a characteristic feature of α-methylfurane. These effects are determined, presumably, by strong interaction between the groups near to the ring and the furane ring.

The intensity of the absorption bands of the CH_2- and CH_3-groups in the standard compounds is given in Table 3; the information is taken from the paper by West et al. [13].

The intensity of the CH_2-groups in the ring is excluded from the total intensity of the absorption bands of the methylene group in the case of compounds of the tetrahydrofurane series. According to our measurements carried out for tetrahydrofurane, $\Sigma I_{CH_2} = 110$ units, i.e., converted to one CH_2-group 27 units. This value is significantly lower than that for cyclanes; e.g., according to published results [2] the intensity of the absorption band of the CH_2-groups in cyclohexane is 89 units calculated in terms of one group.

The intensity of the absorption bands of the methyl and methylene groups is additively dependent on the number of the respective groups both for the furane and tetrahydrofurane series (Table 3).

TABLE 3. Intensities of the Absorption Bands of Methyl and Methylene Groups in Standard Compounds ($I_{CH_3[CH_2]} = \Sigma I_{CH_3[CH_2]}/n$, where n is the number of CH_3 or CH_2 groups; ΔI is the difference between the value and the intensity, relating to one group of the corresponding band in alkanes)

Compound	ΣI_{CH_3}	I_{CH_3}	ΔI	ΣI_{CH_2}	I_{CH_2}	ΔI
α-Methylfurane	24.37	61	–	–	–	–
α-Ethylfurane	69	69	81	36	36	39
α-n-Propylfurane	139	139	11	87	43	32
α-n-Butylfurane	123	123	27	111	37	38
α-n-Amylfurane	142	142	8	195	49	26
α-Methyltetrahydrofurane	90	90	60	–	–	–
α-Ethyltetrahydrofurane	120	120	30	46	46	29
α-n-Propyltetrahydrofurane	150	150	0	142	71	4
α-Isobutyltetrahydrofurane	223	112	–	54	54	21
α-Propyl-β-ethyltetrahydrofurane	290	145	–	170	63	–
α-Ethyl-α'-propyltetrahydrofurane	249	124	–	110	56	–
α-Methyl-α'-propyltetrahydrofurane	234	117	–	140	70	–
n-Alkanes according to [12]	–	150	0	–	75	0

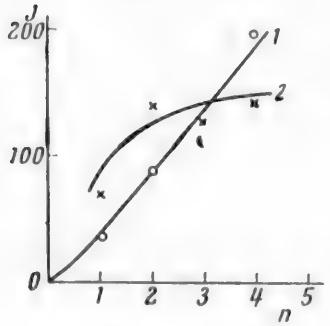

Fig. 1.

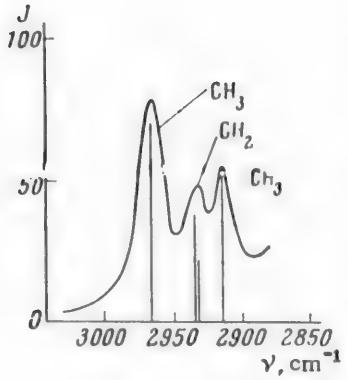

Fig. 2.

An appreciable drop in intensity, as compared with alkanes, is only observed in the first groups nearest to the furane ring. The effect of the tetrahydrofurane ring is significantly weaker.

With further increases in the chain of the alkyl radical the intensity of the absorption bands of the CH_2- and CH_3-groups approximates to the intensity of the corresponding groups in n-alkanes.

Figure 1 shows the relation between the total intensity of the absorption bands of the CH_2-groups in a series of furane compounds and their number (curve 1), and the increases in the intensity of the absorption band of the CH_3-group as its distance from the ring increases for the same compounds (curve 2). The deviation from the corresponding curves observed in some cases can, presumably, be explained by the inaccuracy in resolution of the bands. It should be pointed out that in the case of the tetrahydrofurane series, the effect of the ring on the substituent in the β-position is hardly observable even for groups near the ring. Thus in the case of short alkyl radical having one or two carbon atoms, it is possible to distinguish the position of the alkyl radicals in the tetrahydrofurane ring.

We used the results obtained during studies of standard compounds for determining a number of materials obtained during the alkylation of furane and tetrahydrofurane. Thus, in particular, we established the structure of products later identified as α-methyl-α'-ethylfurane, triethyltetrahydrofurane, and isobutyltetrahydrofurane. The results are given in Table 4. This table includes the intensity of the absorption bands of the CH_2- and CH_3-groups (ΣI_{CH_2}, ΣI_{CH_3}), the number of methyl and methylene groups found n_{CH_3} and n_{CH_2}, and the error in determining the number of groups Δ_n.

Since the spectrum of α-methyl-α'-ethylfurane exhibits a characteristic splitting of the absorption bands of the methyl group, and a shift in the band of the CH_2-group (see Fig. 2) it was possible to establish the type of substitution for this compound.

Results obtained by infrared spectroscopy were confirmed by other physicochemical methods. Thus by introducing the necessary correction, and increasing the intensity of the band to a value found during studies of standard samples, thereby taking into account the drop in intensity for the groups nearest to the ring, methods which have been developed for the alkanes can be successfully applied to the determination of the number of CH_2- and CH_3-groups in furane and tetrahydrofurane compounds.

TABLE 4. Analytical Results for Some Products Obtained during the Alkylation of Furane and Tetrahydrofurane

Compound	ΣI_{CH_3}	ΣI_{CH_2}	n_{CH_3}	n_{CH_2}	Δn_{CH_3}	Δn_{CH_2}
α-Methyl-α'-ethylfurane	56—CH_3 74—C_2H_5	32	1,5 1,1	0,9	0,5 0,1	0,1
Triethyltetrahydrofurane	354	147	2,7	3,2	0,3	0,2
Isobutyltetrahydrofurane	235	54	2,0	1,0	0	0

Notes: 1) The band of the CH_3-group splits into its components. 2) The intensity which is determined by the methylene groups in the tetrahydrofurane ring is excluded from the total intensity of the CH_2-groups.

SUMMARY

It has been shown that it is possible to use the methods for determining alkanes for the determination of the number of methyl and methylene groups in the alkyl radicals in compounds of the furane and tetrahydrofurane series.

The additive character of the relation between the intensity of the absorption bands of CH_2- and CH_3-groups in the infrared spectrum and the number of the corresponding groups has been demonstrated.

The relation between the position and intensity of the absorption bands of CH_2- and CH_3-groups and the position of these groups with respect to the furane and tetrahydrofurane ring has been examined.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

DETERMINATION OF ALIPHATIC ACID HYDRAZIDES BY POTENTIOMETRIC TITRATION WITH SODIUM NITRITE

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 643-644, September-October, 1961
Original article submitted November 10, 1960

A number of methods are known at present for the quantitative determination of aliphatic acid hydrazides [1-4]. We have extended an analytical method for the determination of acid hydrazides by potentiometric titration with sodium nitrite which was suggested earlier for aromatic acid hydrazides [5] to cover the hydrazides of aliphatic acids. The basis of this method is the fact that aliphatic hydrazides also react readily with nitrous acid in a hydrochloric acid medium according to the equation:

$$RCONHNH_2 + HNO_2 \longrightarrow RCON_3 + 2H_2O$$

Aliphatic hydrazides, in contrast to aromatic hydrazides, quantitatively react with nitrous acid only at a strictly defined acidity. This is explained by the fact that in the presence of a large excess of aqueous solutions of mineral acids aliphatic hydrazides hydrolyze to hydrazine and the corresponding acid according to the scheme [1]:

$$RCONHNH_2 \xrightarrow{HOH} RCOOH + N_2H_4$$

Since a molecule of hydrazine interacts with two molecules of nitrous acid according to the equation [6]:

$$N_2H_4 + 2HNO_2 \rightarrow N_2 + H_2N_2O_2 + 2H_2O$$
$$H_2N_2O_2 \rightarrow N_2O + H_2O$$

high results are obtained for such hydrazides.

As the reactivity of the hydrazides decreases the accuracy with which they can be determined decreases. Thus the hydrazides of formic and methoxyacetic acid were determined with an error of up to 10%. On the other hand, the introduction of a phenyl ring into the α-position of aliphatic hydrazides renders such compounds less sensitive to the effect of mineral acids. Like the hydrazides of aryl carboxylic acids they are readily determined over a wide acidity range.

EXPERIMENTAL

The hydrazides of acetic, propionic, butyric, phenylacetic, phenoxyacetic, formic, and methoxyacetic acids were carefully purified; the content of the given preparation in a test sample was about 100%.

The experimental technique was similar to that described previously [7-9]. All experiments were carried out at room temperature. A 0.01 N sodium nitrite solution was used as the titrant, it was standardized potentiometrically against sulfanilic acid [7]. 0.05 M solutions of the hydrazides were prepared by dissolving accurately weighed aliquots in benzene. Hydrochloric acid and KBr were added to 10 ml of the hydrazide solution, titration was then carried out from a 10 ml microburet with 0.02 ml scale divisions, the drawn out tip of this buret being immersed in the solution being titrated. At the beginning of titration the potential was established almost instantaneously; near the end point the potential was established after 50-10 min. Addition of KBr improves the inflection in the potential.

The effect of hydrochloric acid concentration on the accuracy of determination of alkyl hydrazides is evident from the results given in Table 1. The best results are obtained in a medium of 0.03-0.05 M HCl. Results of the determination of aliphatic acid hydrazides are given in Table 2.

The mean result of not less than five determinations is given in the last column. Statistical treatment of the results [10] shows that the experimental accuracy is not less than 1%. The total nitrogen content of all the test hydrazides as determined by the Dumas method confirmed the correctness of the results of the titrimetric method.

TABLE 1. Effect of Hydrochloric Acid Concentration on the Results of Titrating Acetyl Hydrazide with Sodium Nitrite

C_{HCl}, M	Found, %	C_{HCl}, M	Found, %
0,01	106,0	0,30	108,2
0,02	104,9	0,60	110,6
0,03	100,2	1,25	130,1
0,05	100,8	2,50	151,8
0,10	102,8	5,00	193,0
0,15	106,2		

TABLE 2. Determination of Some Hydrazides

Acid hydrazides	Sample wt., mg	Found, %
Acetic	3,70	100,2
Propionic	4,40	99,7
Butyric	5,11	100,4
Phenylacetic	7,51	100,3
Phenoxyacetic	8,31	100,4

The method can also be carried out by a macro variant, the amounts of the reagents being appropriately increased.

EXPERIMENTAL

An aliquot of hydrazide (0.01-0.05 mM) is dissolved in 5-10 ml of benzene in a 50-100 ml beaker; 10 ml of 0.05 N hydrochloric acid and 0.1-0.2 g potassium bromide are added, and a platinum electrode (a quinhydrone or saturated calomel electrode is used as the auxiliary electrode) immersed in the solution.

While the solution is vigorously stirred with a mechanical stirrer 0.01 N sodium nitrite solution is added in definite portions from a microburet (the tip of which is immersed in the liquid). The end point is established on the basis of the maximum $\Delta E/\Delta V$.

SUMMARY

A method has been developed for the quantitative determination of aliphatic acid hydrazides by potentiometric titration with sodium nitrite. It has been shown that aliphatic hydrazides are readily determined (with an error of up to 1%) in a medium of 0.03-0.05 M HCl.

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A COLORIMETRIC METHOD OF DETERMINING PROLINE

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 645-646,
September-October, 1961
Original article submitted November 4, 1960

Several methods are known for the photometric determination of proline. The most widely used of these methods is that of Guest [1]. Nevertheless, apart from the difficulties involved, current methods give inaccurate results. Accordingly, we set ourselves the problem of developing an improved photometric method of determining proline.

The method developed is based on the fact that the reaction product of proline with ninhydrin is readily extracted with isobutanol to give a bright-red colored solution.

The following procedure is adopted for determination of proline in protein hydrolyzates: 1 ml of test protein is hydrolyzed in a boiling water bath for 15 hr with an equal volumeof 4 N hydrochloric acid. The hydrolyzate is then evaporated to dryness to remove most of the hydrochloric acid. Four ml of 3% trichloroacetic acid and 1 ml of 10% phosphomolybdic acid solution are added to the dry residue. The trichloroacetic acid and phosphomolybdic acid are added to remove unhydrolyzed protein and peptones. The residue is filtered off. To 0.5 ml of the filtrate is added 0.5 ml of a 2% aqueous solution of ninhydrin. The mixture is placed for 10 min in a boiling water bath and 50 ml of water are then added.

When hydrochloric acid is present at a concentration higher than 0.1 N a violet color does not appear on boiling the protein hydrolyzate with ninhydrin. But on dropping the concentration only a little further to 0.062 N the color with ninhydrin develops completely; accordingly, a one stage evaporation of hydrochloric acid from the hydrolyzate is sufficient for realizing the color reaction. However, when the hydrolyzates contain traces of hydrochloric acid, the isobutanol extract has a violet not a red color. A relatively large amount of water – 50 ml – is added to the hydrolyzate to destroy the violet tinge, and when this is done the isobutanol acquires a red color.

After adding water to the colored solution, 10 ml of isobutanol is added and the whole carefully shaken for 3 min. After the layers have separated, the upper, alcoholic layer has a bright rose color.

The result obtained is multiplied by 0.5 during calculation of the proline content of the protein hydrolyzates.

Experiment showed that the best results are obtained on working with hydrolyzates containing 80-2000 mg % of proline. The limiting sensitivity of the reaction is 15 mg% proline.

In model experiments with amino acids dissolved in mixtures of trichloroacetic acid and phosphomolybdic acid, it was found that the color of the isobutanol layer is specific for proline and is not observed in the case of solutions of other amino acids: histidine, lysine, tyrosine, tryptophane, phenylalanine, cystine, cysteine, serine, leucine, alanine, glycine, norleucine, glutamic and aspartic acids, and also urea.

The error does not exceed ± 4% in parallel determinations of various amounts of proline in pure solutions. On adding proline to protein hydrolyzates the error rises to ± 12%. The method gives more accurate results than Guest's method (the error in the latter amounts to ± 19%). During precipitation of native protein with phosphomolybdic acid the precipitate entrains some of the phosphomolybdate from solution. Nevertheless, varying final concentrations of phosphomolybdic acid (from 1 to 2.5%) do not affect the color sensitivity.

Formaldehyde (at a final concentration of 1-10%), sulfosalicylic and trichloroacetic acids (at a final concentration of 0.6-0.9%), and ethanol and acetone at concentrations up to 6% do not interfere with proline determination.

The red colored solutions do not conform to Beer's law so that a calibration curve must be used.

The optical density should be measured with a light filter having maximum transmission at 533 mμ for photometric determination of proline.

Boiling proline with 18% hydrochloric acid for 12 hr does not lower the intensity of the color subsequently obtained. Accordingly, hydrolysis does not destroy proline. Alkaline hydrolysis of protein leads to partial destruction of proline. On boiling proline solutions with 0.5 N sodium hydroxide for 12 hr the proline content decreases by 32%.

Proline could not be detected in nonhydrolyzed 10% solutions of casein, gelatin, and crystalline ovoalbumen. Only traces of proline could be detected in the same proteins after they had been subjected to the action of 1% pepsin for 2 hr at 24° in the presence of 1% hydrochloric acid.

TABLE 1. Proline Content of Protein Hydrolyzates as a Percentage of Total Resin taken as 100%

Protein	Proline content, %	
	found	published data
Ovoalbumen	5.1	4-5 [2, p. 368]
Casein	7.5	8, 2 [2, p. 371]
Gelatin	20.5	–
Serum protein	8.0	–

TABLE 2. Determination of Proline in Aqueous Solutions

Proline concentration, mg	Proline found, mg	
	without hydrochloric acid	in the presence of 0.062 N hydrochloric acid
5	5.3	10.6
4	4.0	8.0
3	2.9	5.8
2	2.1	4.2
1	0.9	1.8

Proteins and peptides containing proline do not give a color reaction for this amino acid before hydrolysis. Results of the determination of proline in acid hydrolyzates of 10% solutions of ovoalbumen, casein, gelatin, and also in hydrolyzates of 30 horse antidiptheria sera are given in Table 1.

On adding 5 mg of proline to 1 ml of a protein solution subjected to hydrolysis, all the proline was determined; 10.2% of proline was found in ovoalbumen, 12.4% in casein, and 25.5% in gelatin.

When the proteins to which proline was added were not subjected to hydrolysis, determination of proline was impossible since the nonhydrolyzed proteins were precipitated with phosphomolybdic acid and entrained large amounts of proline. Thus, when the final concentration of casein was 0.6%, it entrained 11% of the proline, while ovoalbumen and gelatin at the same concentrations entrained 54% and 59%, respectively. Complete acid hydrolysis of protein is essential for quantitative determination of proline.

Table 2 contains results of experiments with aqueous solutions of proline with and without hydrochloric acid; the final HCl concentration was 0.062 N.

Table 2 shows that the results obtained during the quantitative determination of proline in pure solutions can be regarded as reasonably satisfactory. The results obtained in the presence of traces of hydrochloric acid are twice those obtained in its absence. This fact must be taken into account when calculating the proline content of protein hydrolyzates.

SUMMARY

The proline content of protein hydrolyzates can be determined on the basis of the intensity of the red colored extract obtained on extracting the reaction product formed between proline and ninhydrin with isobutanol.

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BRIEF COMMUNICATIONS

CHROMATOGRAPHIC SEPARATION OF WEIGHABLE AMOUNTS OF CESIUM AND RUBIDIUM ON KU-1 CATION EXCHANGE RESIN

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 647-648, September-October, 1961
Original article submitted May 31, 1960

The possibility was demonstrated recently [1] of effecting a rapid and efficient separation of unweighable amounts of francium, cesium, and rubidium on the Russian cation exchange resin KU-1. An interesting feature of this separation was the use of hydrochloric acid at a concentration of 5.5 M as eluant; such a concentration had, up to that time, never been used in the practice of ion exchange chromatography for the separation of the alkali metals. The hydrochloric acid concentration normally used for separating mixtures of these elements lies within the limits 0.1-0.3 M [2]. It was of interest therefore to examine the possibility of separating weighable amounts of rubidium and cesium on this cation exchange resin using hydrochloric acid of varying concentrations for this purpose, and, in addition, to study the efficiency of separation for various proportions of these elements in their mixtures.

Only a few papers have been published on the separation of weighable amounts of the heavy alkali metals [3-6]; in some of these papers the methods described are very long and are not always efficient. There is no published information on the effect of the proportions of rubidium and cesium in test mixtures on separation efficiency.

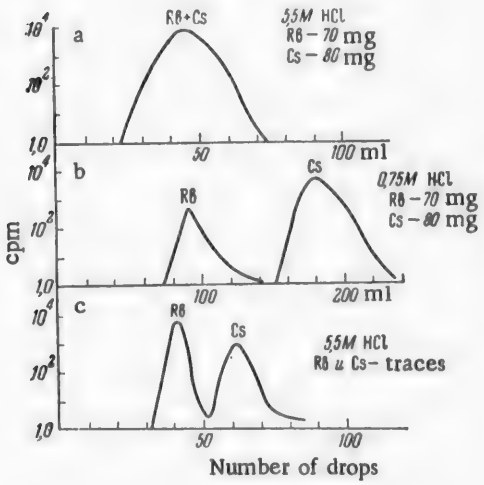

Fig. 1. Elution curves of weighable and trace amounts of Cs and Rb on KU-1 cation exchange resin using HCl solutions of varying acidity.

The method of studying elution of cesium and rubidium labelled with the radioactive isotopes Cs^{134} and Pb^{86} consisted of the following. A column of KU-1 cation exchange resin in the H-form (particle size 150-200 mesh) the column having a diameter of 1 cm and a length of 36 cm was washed with a solution of hydrochloric acid at the test concentration; subsequently 0.1-0.2 ml of an acid solution of the same concentration and containing a mixture of cesium and rubidium was introduced into the top of the column. In order to promote formation of narrow adsorption zones in the column the solution was allowed to pass as slowly as possible along the column, the latter was then eluted with acid of the requisite concentration at the rate of 0.3 ml/min. The solution issuing from the column and having a volume of 1 ml was collected in a test tube and its activity measured on the basis of its β- and γ-radiation respectively on the standard TM-20 counter and on an AMM-4 γ-counter. We decided to use 0.75 and 5.5 M solutions of hydrochloric acid as test eluants; since the greatest difference in the partition coefficients for Rb and Cs, determined under static conditions [11], is observed at these acid concentrations.

Results of experiments on the separation of 80 mg cesium and 70 mg rubidium by means of these solutions are given in Fig. 1, a, b. It follows from this figure that the use of 5.5 M hydrochloric acid as eluant does not even lead to partial separation of cesium and rubidium. Nevertheless, by washing the column with 0.75 M hydrochloric acid we were able to separate these large amounts of rubidium and cesium in about 15 hr. This time can be reduced by passing through the column, after the rubidium has been eluted with 0.75 M hydrochloric acid, an acid solution with a concentration of about 6 M which appreciably accelerates the displacement of the zones of the elements (Fig. 2).

In order to establish the effect of the ratios of weighable amounts of the components on the extent to which they are separated, acid solutions of the concentrations indicated above were used. Results of these experiments are given in Figs. 1 a, b, and 2; it follows from these that separation of both small amounts of one element from predominant amounts of the other for rubidium to cesium ratios of 1:80 and 70:1, as well as separation of mixtures containing 150 mg of these elements at a ratio of about 1:1, is quantitative. This method therefore permits separation of cesium and rubidium in almost any proportion.

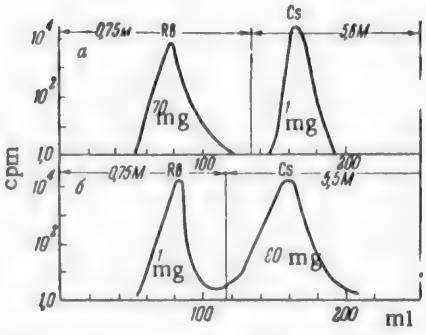

Fig. 2. Elution curves of Cs and Rb for various ratios of these elements in their mixtures.

The fact that weighable amounts of these elements are not separated when they are eluted with high concentrations of hydrochloric acid, while such a separation is effected on eluting with 0.7 M acid solution can be explained by the sharp decrease in the frequency of the elementary acts of sorption and desorption as a consequence of the rapid displacement of the zones of the elements. Nevertheless, the possibility of separating ultrasmall amounts of cesium and rubidium on small columns (10 x 0.3 cm) by means of 5.5 M hydrochloric acid (Fig. 1c) allows one to assume that in addition to the factor mentioned above, the kinetics of the process also affect the efficiency of separation. It is known [2, 7] that the exchange rate is determined by external diffusion in the case of low concentrations, while at high concentrations this rate is determined by internal diffusion. It is obvious that the exchange rate for external diffusion, which is in certain respects identical with the rate of chemical reaction in solution, is higher than in the case of internal diffusion [8, 9]. According to theoretical considerations, in ion exchange chromatography, the increase in the exchange rate of the ions determines the smaller diffuseness of the zones of the elements, i.e., it determines the higher efficiency of separation.

In conclusion, we should like to point out that it would be interesting both from a theoretical and practical point of view to study the efficiency of the separation of rubidium and cesium in the intermediate region between microconcentrations and weighable amounts on eluting with HCl of high concentration.

The author wishes to thank S. S. Rodin for his help in the work.

SUMMARY

A study has been made of the possibility of separating weighable amounts of Rb and Cs, when present in various ratios, on a KU-1 cation exchange resin on eluting them with HCl of varying concentrations. It has been shown that when elution is carried out with 0.75 M HCl, the elements can be effectively separated at the following ratios 1:1, 1:80, and 70:1. When 5.5 M HCl is used for elution, separation of weighable amounts is not observed, though micro amounts of these elements can be separated with acid of this concentration. Some theoretical considerations are advanced to explain these phenomena.

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DESTRUCTION OF ETHYLENEDIAMINETETRACETIC ACID BY OXIDATION WITH HYDROGEN PEROXIDE

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Translated from the Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 649-650,
September-October, 1961
Original article submitted November 29, 1960

Pribil [1] as well as Smirnov-Averin, Krot, and Sokolov [2] have removed sodium ethylenediaminetetracetate (EDTA-Na) from solution by oxidizing it. Pribil oxidized EDTA-Na by boiling it for a long time in a hydrochloric acid medium with potassium chlorate. Smirnov-Averin et al., recommend the use of a twofold excess of potassium persulfate for oxidizing EDTA-Na; the solution should be boiled for 10-15 min. A drawback of this method of destroying EDTA-Na, however, is the formation of appreciable amounts of sulfate ions in solution, an undesireable feature sometimes. In such cases it is more convenient to destroy EDTA-Na by oxidizing it with hydrogen peroxide. It has been established [3] that excess of concentrated hydrogen peroxide oxidizes ethylenediaminetetracetic acid (EDTA) both in acid and in alkali media; on boiling, oxidation of EDTA is quantitative in 3-5 min. In the cold only about 20% is oxidized in the course of 18-20 hr.

Results of oxidizing EDTA-Na with excess hydrogen peroxide in alkali and acid media at different temperatures are given in the table.

Oxidation of EDTA-Na with Hydrogen Peroxide (ten ml of 30% H_2O_2 was added in each case, the final volume of the solution with 100 ml)

Amount of EDTA-Na taken, g	Oxidizing conditions	EDTA-Na found, g	Percentage EDTA-Na oxidized
0.0360	HCl medium, pH < 1; titrated immediately with $MgCl_2$ solution	0.0354	1.6
0.5860	HCl medium, pH < 1; the solution was allowed to stand for 20-22 hr at room temperature	0.440	24
0.3830	Alkali medium, pH > 10; the solution was allowed to stand for 20-22 hr at room temperature	0.292	21
0.4670	HCl medium, pH < 1; the solution was boiled for 3-5 min	0	100
0.5990	Alkali medium, pH > 10; the solution was boiled for 3-5 min	0	100

Experiment showed that in order to achieve complete oxidation of EDTA-Na not less than a tenfold excess of hydrogen peroxide must be added (with respect to the EDTA-Na).

Destruction of EDTA-Na with hydrogen peroxide can be used with success for separating many elements (Fe^{III}, Th, La, etc.) in the form of their hydroxides from solutions containing the complexon.

The compounds formed during the oxidation of EDTA-Na hardly complex Th, Fe^{III}, and La at all and do not interfere with the quantitative precipitation of their hydroxides. A known amount (20-25 mg) of Th, Fe^{III}, or La in the form of their salts was placed in a beaker, excess EDTA-Na was added (70-200 mg) and the solution diluted

with water to 20 ml; the final solution was neutralized with alkali to pH 10-11, 1-2 ml of 30% H_2O_2 was added and the whole boiled for 3-5 min. The solution was cooled, the precipitate of hydroxides was filtered off, washed, dissolved in acid and the amount of Th, Fe^{III}, or La determined quantitatively by titration with EDTA-Na solution according to published methods [4]. In all cases quantitative separation of the elements as their hydroxides was observed.

Presumably, oxidation with hydrogen peroxide could also be used for destroying EDTA-Na during the separation of many other metals as their hydroxides.

SUMMARY

Hydrogen peroxide completely oxidizes sodium ethylenediaminetetracetate on boiling for 3-5 min in both alkali and acid media. Thorium complexonates are broken down under these conditions; this technique can be used when such elements are separated as their hydroxides.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ANALYSIS OF REFRACTORY ALLOYS CONTAINING ZIRCONIUM (TITANIUM) AND TUNGSTEN

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 651-652, September-October, 1961
Original article submitted December 13, 1960

Published methods for separating tungsten from zirconium or titanium [1, 2], e.g., fusion with sodium carbonate and subsequent leaching of the melt with water or 10% sodium hydroxide, do not give good results when the contents of the components are high, even after a double reprecipitation.

The aim of the work described here was to develope a method for separating and determining the elements in TiB_2–WC and ZrB_2–WC alloys. The methods which we studied for separating tungsten and zirconium were: 1) separation with perchloric, nitric, and sulfuric acids; 2) separation with cupferron. Separation with acids did give positive results.

Separation by means of cupferron. Tungsten forms complexes with organic acids, in particular with oxalic acid, which dissociate only to a small extent. Titanium and zirconium also form complexes with oxalic acid, but oxalic acid does not interfere with the precipitation of zirconium and titanium cupferronates [3]. For determining the components of the alloys Ti(Zr)–W we thought it would be of interest to extract zirconium and titanium cupferronates [4-6]. We made use of differences in the stability of the complexes of tungsten and zirconium (titanium) with oxalic acid, and in the extractability of their cupferronates, for separating these metals.

TABLE 1. 0.0831 g ZrO_2 and 0.0881 g WO_3 Taken

Oxalic acid taken, g	ZrO_2 found, g
0.45	0.0831; 0.0829
0.90	0.0828; 0.0830
1.35	0.0830; 0.0836
2.25	0.0817; 0.0786

Initially, we made a study of the solubility of zirconium cupferronate in oxalic acid of varying concentrations, in order to establish the minimum amount of oxalic acid required to complex tungsten in the presence of zirconium. The experiments were carried out as follows. Standard solutions of tungsten and zirconium* were poured together, and varying amounts of a concentrated oxalic acid solution added; the zirconium was then precipitated with cupferron (the total volume of the solution was 100 ml). Zirconium cupferronate was filtered off, washed with water, calcined, and weighed.

It follows from the results obtained (Table 1) that zirconium cupferronate does not dissolve in the presence of 0.5-1 g of oxalic acid (this corresponds to 5-10 ml of its saturated solution); the tungsten is readily kept in solution. An appreciable excess of oxalic acid is undesirable; thus when 2.25 g (25 ml of saturated solution) of oxalic acid is taken, zirconium cupferronate also partially dissolves.

Separation of tungsten and zirconium (titanium) by extraction of the cupferronates was checked initially on synthetic mixtures. These experiments were carried out as follows. Standard solutions of tungsten and zirconium or titanium were introduced into a 150 ml separating funnel, 2 ml of concentrated sulfuric acid and 5-10 ml of saturated oxalic acid solution were added and the liquid diluted to 70 ml with water; titanium or zirconium were then precipitated with a 6% aqueous solution of cupferron (7-10 ml). The cupferronate was extracted 2-3 times with chloroform (10, 5, and 5 ml).

After separation, tungsten remains in solution as its oxalate complex; zirconium and titanium pass into the chloroform layer.

Tungsten was determined in the aqueous solution by precipitation with 8-hydroxyquinoline [2, 7]. The solution was neutralized with 20% sodium hydroxide or ammonia to a neutral end point, 15 ml of 2 M sodium acetate

*Solutions were prepared from powders of the pure metals. The solutions were standardized gravimetrically.

was then added – the pH of the solution should be 5 (test with universal indicator paper). Tungsten was precipitated with an acetic acid solution of 8-hydroxyquinoline, the solution was heated to coagulate the precipitate which was filtered off on ashless filter paper (white band) using macerated paper (filter aid). The precipitate was washed 5-6 times with hot water, dried, calcined, and weighed as WO_3.

Titanium was determined in the chloroform layer as follows. Chloroform was removed by gentle evaporation on a water bath or distilled off. The cupferron was destroyed by boiling with a mixture of nitric and sulfuric acids; the mixture was heated until white fumes of sulfuric acid appeared. On cooling, the residue was diluted with water and precipitation effected with cupferron. Results of tungsten and zirconium (titanium) determination, after their separation, are given in Table 2.

TABLE 2.

WO_3 taken, g	WO_3 found, g	TiO_2 taken, g	TiO_2 found, g	ZrO_2 taken, g	ZrO_2 found, g	WO_3 taken, g	WO_3 found, g	TiO_2 taken, g	TiO_2 found, g	ZrO_2 taken, g	ZrO_2 found, g
0,0250	0,0250	0,0140	0,0138	—	—	0,1000	0,0997	0,0420	0,0424	—	—
0,0375	0,0377	0,0210	0,0212	—	—	0,0705	0,0704	—	—	0,0533	0,0535
0,0500	0,0503	0,0280	0,0284	—	—	0,0705	0,0708	—	—	0,0533	0,0534
0,0625	0,0619	0,0350	0,0349	—	—	0,0705	0,0708	—	—	0 0533	0,0533

TABLE 3.

Sample No.	W found, %	W found by the method of additions, %	Ti found, %
1	32,3; 32,2	32,5	48,6; 48,5
2	37,9; 37,7	37,7	43,5; 43,4

As the results given in Table 2 show, by extracting titanium and zirconium cupferronates in the presence of oxalic acid, it is possible to achieve a satisfactory separation of these elements from tungsten, and to determine them separately.

Determination of tungsten and titanium in TiB_2–WC alloys. On the basis of the experiments carried out on synthetic mixtures the following method is suggested for determining titanium (zirconium) and tungsten in alloys.

A 0.1 g aliquot of alloy is dissolved in a mixture of hydrofluoric and nitric acids contained in a platinum basin; sulfuric acid is added, and the mixtures heated to the appearance of white fumes of sulfuric acid. The cooled solution is diluted with water and transferred to a separating funnel; subsequently oxalic acid and cupferron are added. The cupferronate is extracted and the method outlined above for the analysis of synthetic mixtures then followed. Table 3 contains results obtained during the determination of tungsten and titanium in TiB_2–WC alloys.

In order to check on the method, the components of the alloy were determined by the method of additions; satisfactory results were obtained.

SUMMARY

A method has been developed for the determination of titanium (zirconium) and tungsten in TiB_2–WC and ZrB_2–WC alloys. It is based on separation of the elements by precipitation of titanium or zirconium cupferronates in the presence of oxalic acid which masks the tungsten, and extraction separation of the cupferronates followed by determination of tungsten with 8-hydroxyquinoline, and titanium and zirconium by a gravimetric cupferron method.

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A COMPLEXOMETRIC METHOD FOR THE DETERMINATION OF PHOSPHORUS*

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 653-654, September-October, 1961
Original article submitted November 10, 1960

Practical demands for an accurate method which is less difficult than the gravimetric method for determination of phosphorus in phosphoroorganic compounds led us to carry out a careful check on a complexometric method for the determination of orthophosphate. For study we chose the simplest method based on precipitation of PO_4^{3-} as $MgNH_4PO_4$ with subsequent determination of the magnesium in the latter by a back complexometric titration [1-5]. On using the normal method for complexometric determination of phosphates [1, 5] involving a single precipitation of $MgNH_4PO_4$, it was found that the results for orthophosphate determination were not reproducible and were very high. The relative error amounted to +5.0%. Modifying the precipitation conditions for $MgNH_4PO_4$ [precipitation temperature, amount of excess magnesia mixture, ammonium chloride concentration, addition of sodium ethylenediaminetetracetate (EDTA-Na)] does not lead to satisfactory results [4-6]. Moreover, during back titration of excess EDTA-Na with a magnesium salt using eriochrome black T as indicator, the color change is less distinct than during direct titration. The color change is observed over a range of 0.10-0.12 ml on titrating with 0.1 N magnesium salt solution.

TABLE 1. Complexometric Determination of Orthophosphate

P_2O_5, mg				Mean error relative, %
taken	found			
165,8	166,1;	165,0;	165,1	—0,2
186,6	186,0;	186,1;	186,6	—0,21
207,3	208,0;	208,1;	207,6	+0,29
228,0	227,6;	228,2;	228,6	+0,04
248,8	248,1;	248,1;	249,3	—0,12

Experiments showed that by carrying out a double precipitation of magnesium ammonium phosphate, and also by titrating with a mixed indicator, accurate and reproducible results can be obtained for orthophosphate.

The use of a mixture of eriochrome black T with methyl orange or methyl red as a mixed indicator has been described [7, 3]. In the work described here we used a mixture of eriochrome black T and p-nitrosodimethylaniline as the mixed indicator for the complexometric titration of magnesium, this mixed indicator gives a distinct color change from green to reddish. Before completion of titration a gradual weakening of the green color is observed. At the end point, on adding the last 0.02-0.04 ml of 0.1 N magnesium salt solution, the green color changes distinctly to reddish. p-Nitrosodimethylaniline does not affect titration. Results for phosphate determination are most accurate when the EDTA-Na solution is standardized against an aliquot of potassium dihydrogen phosphate using the same technique as in an actual determination.

Table 1 contains results for the complexometric determination of orthophosphate using the new indicator — mixture of eriochrome black T and p-nitrosodimethylaniline — and a double precipitation of $MgNH_4PO_4$ and an EDTA-Na solution whose normality had been established against an aliquot of potassium dihydrogen phosphate.

EXPERIMENTAL

150-250 mg of $MgNH_4PO_4$ after the usual reprecipitation and standing, is filtered through a No. 3 or No. 4 glass filter, thoroughly washed with 2.5% ammonia solution and dissolved in 30-35 ml of hydrochloric acid 1:5. The filter is carefully washed with twice distilled water. Fifty ml of 0.1 N EDTA-Na is added to the filtrate and the solution is then made alkaline with concentrated ammonia to the blue color of litmus paper. Fifteen ml of ammoniacal buffer solution, with pH 10 is added and the solution diluted to 200-250 ml with twice distilled water. The solution is cooled to 5-10° and a solid mixture of eriochrome black T and NaCl (1:500) added on a knife tip until a moderate blue color develops, 8-10 drops of 0.005% aqueous p-nitrosodimethylaniline is then added until

*We wish to thank R. N. Golovat for valuable advice given in the course of this work.

an emerald-green color is obtained. The solution is titrated with 0.1 N magnesium salt solution until the green color has disappeared completely and a reddish color is obtained. The magnesium salt solution is standardized by titrating with EDTA-Na solution using the mixed indicator, the EDTA-Na solution having been standardized against an aliquot of potassium dihydrogen phosphate.

The method developed has been used for determining phosphorus in phosphoroorganic compounds. An aliquot of the phosphoroorganic compound was oxidized with a mixture of hydrogen peroxide (free from phosphates) and concentrated sulfuric acid; PO_4^{3-} ions were precipitated as $MgNH_4PO_4$ and after reprecipitation of the latter, determination was carried out as described above. When less than 100 mg of $MgNH_4PO_4$ was obtained, 0.05 N solutions of EDTA-Na and magnesium salt were used.

TABLE 2. Determination of Phosphorus in Some Phosphoroorganic Compounds

Compound	P, %	
	calc.	found
$(C_2H_5O)_2P(S)SK$	13,81	13,78; 13,77; 13,76; 13,82; 13,80; 13,85
$[(i—C_3H_7O)_2P(S)S]_2$	14,52	14,58; 14,50; 14,57
$(C_6H_5O)_2P(S)SH$	10,97	10,93; 10,94
$(C_6H_5O)_2P(S)SK$*	9,67	9,70; 9,65; 9,71

*M. p. 187-188°. This compound was prepared by the interaction of O,O-diphenyldithiophosphoric acid and K_2CO_3 in an ether medium. The product was purified by precipitation with benzene from concentrated acetone solutions.

The method gives readily reproducible results. The accuracy is about 0.3% (relative). Table 2 contains the results for phosphorus determination in some carefully purified phosphoroorganic compounds.

SUMMARY

A more precise complexometric method of determining PO_4^{3-} has been applied to the determination of phosphorus in organic compounds. Results with a relative error of 0.3% have been obtained on reprecipitating the $MgNH_4PO_4$ precipitates, standardizing the EDTA-Na solution used against orthophosphate, and using a mixed indicator consisting of eriochrome black T and p-nitrosodimethylaniline.

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REVIEWS AND BIBLIOGRAPHY

ORGANIC REAGENTS IN ANALYTICAL CHEMISTRY

Transactions of the Commission on Analytical Chemistry, Academy of Sciences of the USSR, Volume XI. 462 pp. Izd. AN SSSR, Moscow, 1960. Printing 4000. Price 20 rubles (old denomination).

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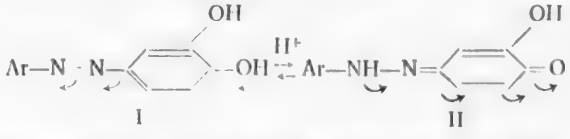
Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 5, pp. 655-656, September-October, 1961

Volume XI of the Transactions of the Commission on Analytical Chemistry is a collection consisting of 47 articles by different authors on problems relating to the theory of the action of organic reagents and their use in analysis. The articles are divided into three sections: 1) theoretical research and study of organic reagents; 2) methods for determination of individual elements; and 3) different applications of organic reagents. The contents of the articles do not always justify the basis for such a strict subdivision.

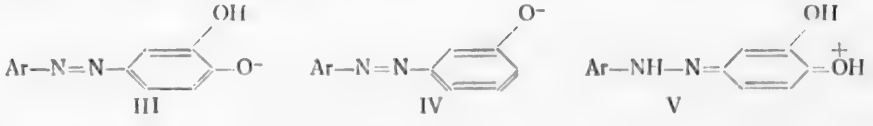
In the opening article of the symposium, "The Effect of the Nature of the Chromophore on Functional-Analytical Groups," the author of the article, M. Z. Yampol'skii, correctly points out the deficiency of the concept of functional-analytical groups for explaining the mechanism of color reactions without taking into account the nature of the chemical bond in the reagent molecule. Nevertheless, the effect of a chromophore on the capacity of an organic compound to be a color reagent for a metal ion is only stated in the article, and is not subjected to actual consideration. The author still adheres to the abandoned concept of the chromophore as a coordinately-unsaturated atom, which did not allow him to come to the obvious conclusion that an organic compound can give a color reaction with a metal ion, only when the reactive group of the reagent closely adjoins the conjugated chain of the chromophore or is a part of the latter.

V. I. Kuznetsov in the article "The Mechanism of Acid Decomposition of Complex Salts," considers phenomena observed in solutions of colored cyclic salts on increasing the hydrogen ion concentration. On slow acidification of a solution of a colored cyclic salt with a strong mineral acid, the color gradually approximates to that which is characteristic for a strongly acid solution of the reagent. When, however, the mineral acid is added rapidly, the color deepens strongly, this color being stable for a more or less prolonged period. Considering the difference between the color of a cyclic salt and that of a reagent as a consequence of intramolecular ionization, V. I. Kuznetsov explains this phenomenon by the fact that "acid decomposition of cyclic salts is preceded by a state with a very strongly manifested intramolecular ionization." This explanation, which is, unfortunately, based on qualitative visual observation, is not convincing. The phenomenon observed can also be explained from another viewpoint. In all the numerous examples given in the article, the reagents used are hydroxyazo compounds for which tautomeric hydroxyazo–quinohydrazone transformations leading to a simultaneous change in the chromophore and reactive group are characteristic, e.g., for derivatives of 3,4-dihydroxyazobenzene (I, II).



I II

Compound II which possesses a carbonyl oxygen with an unshared electron pair, is more capable of forming a coordination bond with a metal ion than in compound I. During rapid decomposition of the cyclic salt formed by compound II, there immediately appears a large amount of unstable molecules of this compound, while its color, as is quite evident, will not be identical with the color of compound I or ions III and IV existing in alkaline media, and of ion V existing in a strongly acid medium



III IV V

In passing, we should point out that not only this case, but often other phenomena which are explained from the position of the hypothesis of intramolecular ionization, or where this theory is used as a basis, can be given other interpretation which are more in line with modern color theory. It is quite obvious that the "hypothesis of intramolecular ionization" requires quantitative physicochemical proof.

In another article "The Mechanism of the Color Reactions of Boron with Hydroxyanthraquinones," V. I. Kuznetsov establishes that in a medium of almost concentrated sulfuric acid, boron reacts with hydroxyanthraquinones as a cation. This fact explains the resemblance of the boron reaction with similar reactions of other multivalent elements undoubtedly present in strongly acid media as cations (germanium, zirconium). However, what was said in the previous instance is also applicable to a certain extent, to the further explanation of the mechanism of the color reactions of boron with hydroxyanthraquinones in concentrated sulfuric acid. Reactions of boron with hydroxyanthraquinones are preceded by a change in the chromophore of the latter caused by the breaking of the hydrogen bond between the carbonyl oxygen and the hydroxy group in the α-position. The explanation of the mechanism of the color reactions of boron with hydroxyanthraquinones given in the article by P. N. Palei, A. A. Nemodruk, and Z. I. Pyzhova in the second section of the symposium (p. 227) is also insufficient, since the authors consider that the complexing agent is not the boron cation, but metaboric acid, and they do not take into account the preceding reaction of the change in the chromophore of the reagent, while the color change is ascribed only to polarization of the bond of the central atom with the hydroxyl oxygen of the addendum. One cannot deny the effect of intramolecular ionization or bond polarization on the color of the intra complex compound. But, however strongly these effects may be manifested, the reason for the development of "not-comparable" colors are not these phenomena, but the preceding reactions involving changes in the chromophore of the organic reagent.

In V. B. Avilov's article the author points out that during potentiometric studies of complex formation between metal ions and the anions of weak organic acids, a correct characteristic of the behavior of redox systems in actual cases is only possible when one takes into account the effect of all the reagents used, in particular that of the strong acids, on the potential of the system.

Taking phenolphthalein as an example, I. G. Shafran critically examines the theory of the use of one-color indicators and defines theory more accurately in the case where a doubly charged indicator ion is colored.

A large group of articles in the first section is devoted to consideration of the analytical properties of, and the application of individual groups of organic reagents. As examples of a quantitative approach to the study of organic reagents, of particular interest is the work carried out by V. M. Peshkova and A. P. Zozulin, and also by A. L. Gershuns; while the work carried out by A. I. Cherkesov serves as an example of the search for reagents on the basis of modern theories of the structure and color of organic compounds, and the work of A. I. Busev and M. I. Ivanyutin for the wide range of materials studied.

The article by I. M. Korenman, A. A. Tumanov, and Z. V. Krainova which ends the first section of the syposium, demonstrates the simplicity and applicability of the radioactive isotopes method for studying precipitation and coprecipitation of elements by the action of organic precipitants, the hydroxyquinolates of zirconium, copper, and cobalt being taken as test examples.

Articles on the use of organic reagents for determination of individual elements are collected in the second section. These articles are devoted to new reagents or to new uses of already known reagents. We should like to mention in particular one of the articles included in this section, an article devoted to a comparative study of methods for determining traces of aluminum by means of organic reagents (L. A. Molot, I. S. Mustafin, and N. S. Frumina). In recent years, unfortunately, similar work has been published more and more rarely. In the meantime a critical evaluation of new reagents and methods of determination appearing in large numbers has become pressingly urgent, since the analytical chemist will simply become confused, unless the new methods are not based on a critical evaluation of the possible variants, as has been done in the article by A. K. Babko and L. V. Markova which deals with reactions for sulfate ions (p. 309).

The third section includes a short article by R. Přibil on new achievements in complexometry with new and interesting examples from an analytical point of view of the selectivity of complexometric determinations. This section also includes reviews of the use of organic reagents in amperometry (V. M. Vladimirova), polarography (S. I. Sinyakova), and chromatography (F. M. Shemyakin). The reviews give a good idea of the possibilities of the use of organic reagents in these respective fields of analysis, but, unfortunately the literature covered in these fields only extends to 1956.

In an article on the selectivity of ion exchange resins, M. M. Senyavin, G. M. Kolosova, and A. B. Pashkov consider the physicochemical processes which occur during ion exchange, and show that the selectivity of the action of ion exchange resins is determined not only by the nature of the functional groups but also by the structure of the sorbent.

The third section also includes several articles on the use of organic reagents for the determination of organic compounds: ethylene oxide (E. Sh. Groisberg); dinitroethylene glycol (A. A. Belyakov); aniline, methylaniline, and dimethylaniline (A. A. Belyakov and N. V. Gorbyleva); esters of p-nitrobenzoic acid (L. P. Kuliev and P. V. Kristalev), air contaminating products from the industrial production of carbon tetrachloride (A. Ya. Tubina); practical recommendations are given. The disproportionately small number of articles from this section included in the symposium only serves to emphasize that the analytical research worker has not hitherto given due attention to this important branch of analytical chemistry.

It is impossible in such a short review to characterize sufficiently fully about fifty various articles. Each of them is of more or less theoretical or practical interest. The symposium will be useful for chemists working in the respective fields.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. –Publisher.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) / Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
Life Sciences		Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
Life Sciences		Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
Chemical Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
Chemical Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
Chemical Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
Earth Sciences		Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
Earth Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
Earth Sciences		Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
Mathematics		Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
Physics		Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
Physics		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series			
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series			
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series			
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology			
	Kinetika i kataliz	Kinetics and Catalysis			
	Koks i khimiya	Coke and Chemistry USSR			
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal			
	Kristallografiya	Soviet Physics – Crystallography			
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals			
	Metallurg	Metallurgist			
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels			
Mikrobiol.	Mikrobiologiya	Microbiology			
OS	Optika i spektroskopiya	Optics and Spectroscopy			
	Pochvovedenie	Soviet Soil Science			
	Priborostroenie	Instrument Construction			
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques			
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics			
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North			
Radiotekh.	Radiotekhnika	Radio Engineering			
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics			
	Stanki i instrument	Machines and Tooling			
	Stal'	Stal (In English)			
Stek. i keram.	Steklo i keramika	Glass and Ceramics			
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production			
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications			
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals			
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)			
UKh	Uspekhi khimii	Russian Chemical Reviews			
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys			
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology			
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal			
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion			
Vop. onk.	Voprosy onkologii	Problems of Oncology			
Vop. virusol.	Voprosy virusologii	Problems of Virology			
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory			
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR			
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics–JETP			
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry			
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology			
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry			
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1 1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1 1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1 1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1 1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1 1958
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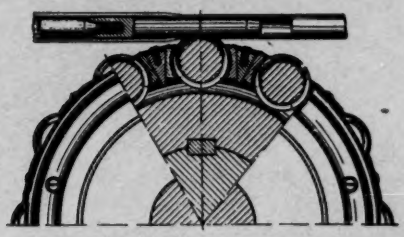
Published by Consultants Bureau
for the Board of Governors of Acta Metallurgica
under a grant from the National Science Foundation



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Edited by A. M. Samarin

TRANSLATED FROM RUSSIAN

(Original published by the Academy of Sciences USSR Press)

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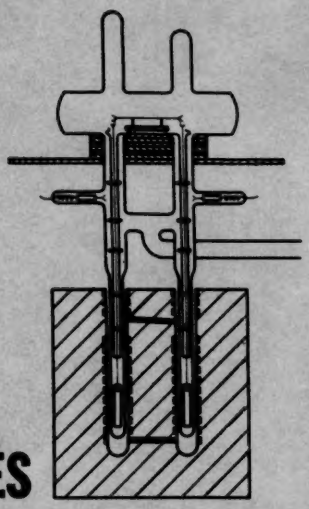

VOLUME I

VACUUM MICROBALANCE TECHNIQUES

Proceedings of the 1960 Conference Sponsored by
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